THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. L APRIL 1955 No. 4

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SUBSCRIPTION: Members $12.00 a Year Non-Members $15.00

Published Monthly by

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLICATION OFFICE, EASTON, PA.

Entered as Second-Class Matter at Post Office, Easton, Pa.
Acceptance for Mailing at Special Rate of Postage as Provided for in Section 1103.
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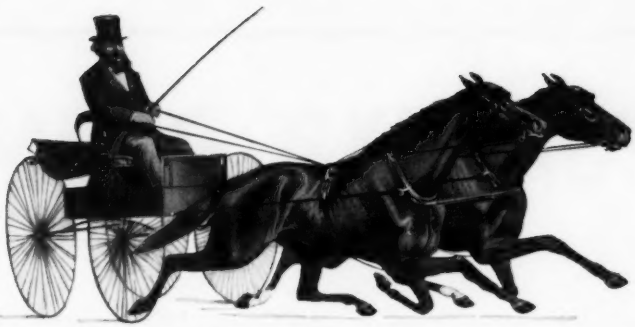
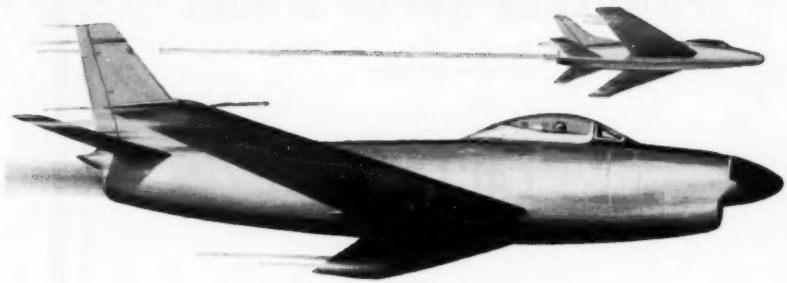


1866...FROM HORSE AGE TO JET AGE...1955



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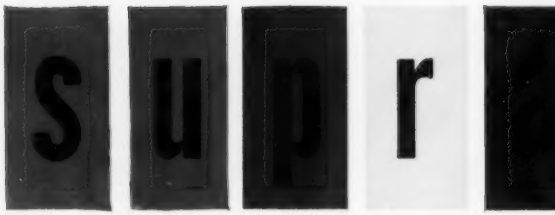

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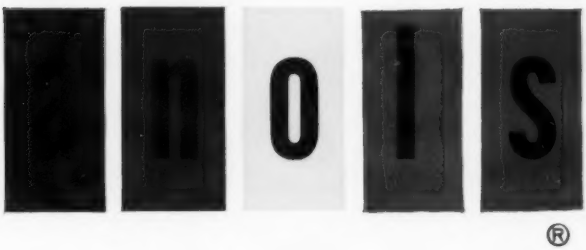

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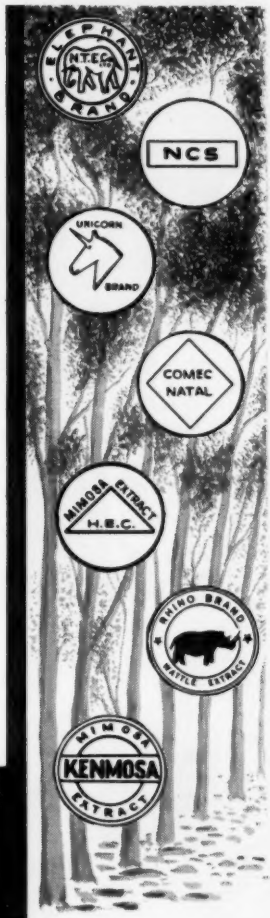

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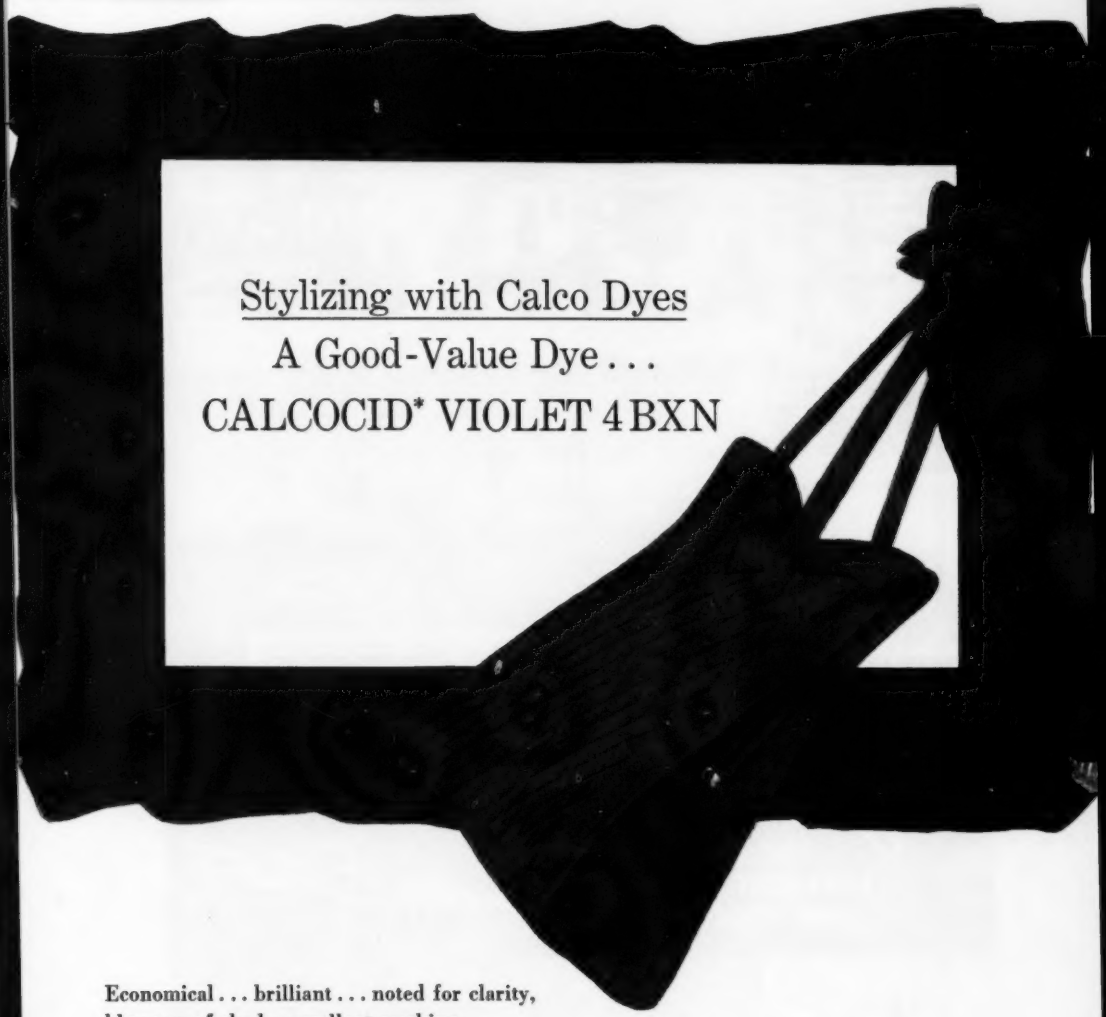

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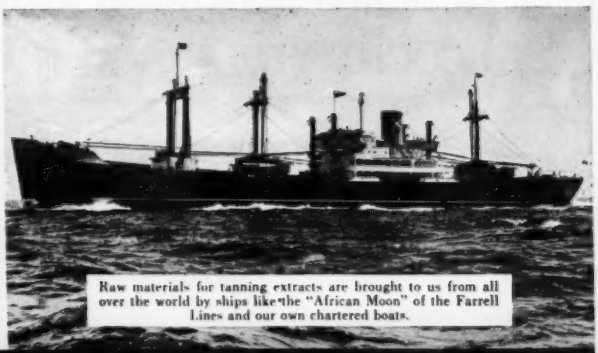

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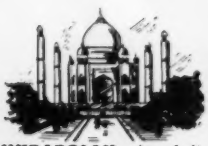

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JOURNAL OF THE
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Vol. L APRIL 1955 No. 4

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Checks for subscriptions and advertisements should be made payable to the American Leather Chemists Association.

Subscriptions—Members, $12.00 annually; Non-members, $15.00 annually.

Published monthly by the American Leather Chemists Association.

Entered as Second-class Matter at the Post Office at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

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G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VETCH, W. K. ALSOP, L. E. LEVI, C. R. OBERFELL, R. W. GRIFFITH, C. C. SMOOT, III, J. S. ROGERS, LLOYD BALDERSTON, J. A. WILSON, R. W. FREY, G. D. McLAUGHLIN, FRED O'FLAHERTY, A. C. ORTHMANN, H. B. MERRILL, V. J. MLEJNEK, J. H. HIGHBERGER, DEAN WILLIAMS, T. F. OBERLANDER, A. H. WINHEIM, R. M. KOPPENHOEFER, H. G. TURLEY.

OFFICERS 1954-'55

President—E. S. Flinn, Ardslea, Route 8 Chillicothe, Ohio.

President-Elect—E. B. Thorstensen, S. B. Foot Tanning Company, Red Wing, Minnesota.

Secretary-Treasurer—Fred O'Flaherty, Department of Leather Research, University of Cincinnati, Cincinnati, Ohio.

Council

R. G. Heinrich, B. D. Eisendrath Tanning Company, Racine, Wisconsin.

H. R. Wilson, B. D. Eisendrath Memorial Laboratory, 702 Racine Street, Racine, Wisconsin.

J. R. Kanagy, 9922 Sutherland Road, Silver Spring 5, Maryland.

Mieth Maeser, United Shoe Machinery Corporation, Research Division, Balch Street, Beverly, Massachusetts.

Dominic Meo, Jr., Salem Oil and Grease Company, Salem, Massachusetts.

BUREAU OF EMPLOYMENT

Position Wanted: Chemist-Tanner wants position in Tanning Industry. Man of mature experience in all phases of chrome and vegetable tanning – especially mechanical use leathers such as textile, lace, transmission belting, packing, washers and hair on leathers. Graduate engineer with many years of experience in technology and plant operations. Address replies to Box BT200, c/o Secretary of A.L.C.A., University of Cincinnati, Cincinnati 21, Ohio.

Leather manufacturers with factories in Britain and on the continent of Europe require experienced technical manager specialist in producing full chrome goat suedes with knowledge of grain garment leather. Italian speaking or prepared to learn it, also if possible English or German. Capable of taking charge of complete production and factory administration. Address replies to Box AH200, c/o Secretary of A.L.C.A., University of Cincinnati, Cincinnati 21, Ohio.

ELECTION TO ACTIVE MEMBERSHIP

Robert G. Banner, Diamond Alkali Company, Diamond Technical Center, Painesville,Ohio.
Jose Behar B., Ave. la, esq. 12, Apt. 1, Miramar, Havana, Cuba.
Raymond N. Berg, 51 N. Main Street, Pine Grove, Pennsylvania.
Eduardo Bernal, Apartado Nacional 2502, Bogota, Columbia.
Johan Bjorksten, Bjorksten Research Laboratories, 323 West Gorham Street, Madison 3, Wisconsin.
Chester E. Claff, Jr., B. B. Chemical Company, 784 Memorial Drive, Cambridge 39, Massachusetts.
Charles R. Clark, K. J. Quinn & Company, Inc., 195 Canal Street, Malden, Massachusetts.
Ross G. Donovan, Box 1175, Aurora, Ontario, Canada.
Edward M. Filachione, Eastern Utilization Research Branch, U. S. Department of Agriculture, Philadelphia 18, Pennsylvania.
Richard N. Jones, 74 County Road, Reading, Massachusetts..
Merton D. Minsky, 578 North Elm Street, W. Bridgewater, Massachusetts.
Perley Payson, Jr., 34 Channing Street, Wollaston 79, Massachusetts.
Carl A. Powers, 59 Halstead Street, Hurtsville, N.S.W., Australia.
Richard D. Prime, Rohm and Haas Company, 25 Beale Street, Room 443, San Francisco, California.
Herbert A. Tetreault, 4 Longfellow Road, Lexington 73, Massachusetts.
Robert F. Welch, Prime Leather Finishes Company, 188 South Second Street, Milwaukee 4, Wisconsin.

TRANSFERRED FROM ASSOCIATE TO ACTIVE MEMBERSHIP

Thomas Aldrich, Marden-Wild Corporation, 500 Columbia Street, Somerville 43, Massachusetts.
Clinton E. Armstrong, 363 Glengrove Avenue, West Toronto, Ontario, Canada.

C. H. Baker, International Shoe Company, 1509 Washington Avenue, St. Louis 3, Missouri.
Angus E. Barton, Robson Leather Company, Ltd., Oshawa, Canada.
Harold Bernard, G. Levor & Company, Inc., Gloversville, New York.
Donald C. Bundy, Northwestern Leather Company, Sault Ste. Marie, Michigan.
James E. Byron, W. D. Byron & Sons Inc., Williamsport, Maryland.
Jerome M. Cohen, Allied Kid Company, Eleventh and Poplar Streets, Wilmington 99, Delaware.
Benjamin W. Crago, L. H. Hamel Leather Company, Haverhill, Massachusetts.
David W. Crookall, Atlas Refinery, Inc., 142 Lockwood Street, Newark 5, New Jersey.
Kenneth W. Folger, Chemtan Company Laboratory, 21 East Hollis Street, Nashua, New Hampshire.
Gerald Glotzbecker, The Raser Tanning Company, Ashtabula, Ohio.
William Hammell, Albert Trostel & Sons Company, Milwaukee 1, Wisconsin.
Raymond Hirsch, Geigy Dyestuff Corporation, 89 Barclay Street, New York 8, New York.
Francis K. Keirnan, 11 Wildemere Terrace, Concord, New Hampshire.
Robert B. Kernahan, 30 Woodlawn Avenue, Coudersport, Pennsylvania.
Fred Klimpl, 412 Sairs Avenue, Long Branch, New Jersey.
Adam M. Lammert, 39 Grapevine Road, Wenham, Massachusetts.
Leon W. Sidebottom, 490 Brook Road, Milton 87, Massachusetts.

ELECTION TO ASSOCIATE MEMBERSHIP

Arthur B. Carlson, Jr., Johnson & Carlson, 848 Eastman Street, Chicago 22, Illinois.
Earl J. Chia, 18 Lane 114, Sec. II, Hoping East Road, Taipei, Formosa.
Cheng-siang Loh, c/o Tai-chung Agriculture College, Tai-chung, Formosa.
Robert L. Melton, Jr., 1226 Washington Street, Grand Haven, Michigan.
M. Nestvold, M. & E. Omdahl A/S, Drammen, Norway.
Thomas D. Nevins, Consulting Engineer, 50 Church Street, New York 7, New York.
Thomas F. O'Brien, Sandoz Chemical Works, Inc., 61 Van Dam Street, New York 13, New York.
George Payne, Benjn. R. Vickers & Sons, Ltd., 5 Grosvenor Road, Hyde Park, Leeds 6, England.
William T. Rossiter, Dow Corning Corporation, Midland, Michigan.
William S. Shore, Eagle-Ottawa Leather Company, 200 N. Beech Tree, Grand Haven, Michigan.
Martin D. Singer, 4 Palmer Avenue, Peabody, Massachusetts.
William Skelly, c/o American Dyewood Company, 374 Main Street, Belleville 9, New Jersey.
Robert A. Ward, 177 Albert Street, Waterloo, Ontario, Canada.

COUNCIL MEETING MINUTES
AMERICAN LEATHER CHEMISTS ASSOCIATION

FEBRUARY 11, 1955
CHILLICOTHE, OHIO

The meeting was held in the conference room at the Mead Corporation Research Laboratory. The meeting was called to order by President Flinn at 10:00 A.M. All Council officers and members were present except Messrs.

Wilson and Henrich. Messrs. Wederbrand, Williams and Telander were also present.

The minutes of the meeting on November 19, 1954, at Cincinnati were approved as published.

President-Elect Thorstensen, as Co-ordinator of Technical Committees, presented the following committee composition, which was approved by Council.

Vegetable Leathers – ARTHUR N. KAY, *Ch.*

Members -

R. G. ASHCRAFT	G. W. SCHULTZ	J. F. WAGONER
H. B. MERRILL	S. DAHL	H. R. MILLER, JR.
G. V. DOWNING	I. D. CLARKE	

Sub-Committees:

Tannin Analysis – ARTHUR N. KAY, *Ch.*

Members –

R. B. BARNWELL	F. F. MARSHALL	J. F. WAGONER
M. BAUM	R. L. MOORE	DEAN WILLIAMS
T. BLAIR	L. W. MORROW	J. JANY
J. H. DAVIS	E. L. RAYFIELD	I. D. CLARKE (non-voting)
G. V. DOWNING	L. SHEARD	C. G. TELANDER (non-voting)
F. P. LUVISI	G. W. STANBERY	J. W. WOLFE (non-voting)

Determination of Lignosulfonates – S. DAHL, *Ch.*

Nontannins in Lignosulfonates, F. F. MARSHALL, *Ch.*

Hide Powder – I. D. CLARKE, *Ch.*

Members —

G. V. DOWNING	G. W. STANBERY	F. F. MARSHALL (non-voting)
G. W. SCHULTZ	A. N. KAY	

Tannery Practices – J. F. WAGONER, *Ch.*

Members –

G. A. BUTZ	J. W. HARNLY	E. H. STEIN
W. C. CURTIN	M. M. LUCKENS	J. E. TARMAN
B. A. GROTA, JR.	E. E. PRESLEY	

Mineral Tanned Leathers – Robert S. Adams, *Ch.*

Members –

Robert Stubbings, N. C. Benrud, Tom S. Perrin, Jesse Wendkos, Richard N. Williams, Titus Weaver, Ludwig Seligsberger

Sub-Committee:

Determination of Zirconium in Leather – J. Wendkos, *Ch.*

Physical and Mechanical Properties – Mieth Maeser, *Ch.*

Sub-Committees:

Physical Testing – Mieth Maeser, *Ch.*

Members –

George Downing, Frank F. Marshall, Seymour Kremen, J. H. Gregory, E. G. Railo, Robert Shaw, J. R. Kanagy, William T. Roddy, Ira D. Clarke, Arthur N. Kay, Jerome S. Rogers

Fastness of Colored Leathers to Light – Ell Dee Compton, *Ch.*

Members –

Robert Shaw, Charles K. Knisely, E. G. Railo, Hans Haemisegger

Water Penetration – R. M. Lollar, *Ch.*

Members –

J. R. Kanagy, Charles W. Mann, Ira D. Clarke, Mieth Maeser

Sampling – Charles W. Mann, *Ch.*

Members —

J. R. Kanagy, Ira D. Clarke, Jerome S. Rogers

Preparatory and Post Tanning Processes – William Roddy, *Ch.*

Sub-Committee:

Fats and Oils – R. M. Koppenhoefer, *Ch.*

Members –

Ben A. Grota, Jr.	Clinton E. Retzsch	George Somer
Robert Hague	C. A. Ross	

Standards and Specifications – Carl G. Telander, *Ch.*

Members –

R. G. Ashcraft	Kenneth H. Knight	Ben A. Grota, Jr.
G. Arthur Brown	Robert M. Lollar	M. H. Battles
Sverre Dahl	Charles W. Mann	R. L. Young
Arthur N. Kay	E. E. Presley	

Leather Finishes – Bernard Roll, *Ch.*

Members –

R. G. Ashcraft	Al Fleisch	Robert Shaw
C. Paul McKee	Titus Weaver	Robert Welch
Elwood Presley	C. David Wilson	

International Committees Composed of Commissions:

International Hide Powder Commission – Ira D. Clarke

International Leather Analysis Commission –

Chemical – Carl G. Telander
Physical – Mieth Maeser

International Tannin Analysis Commission – Arthur N. Kay

It was the wish of Council that a copy of the above listing be sent to each committee chairman.

It was authorized by Council that a certificate of committee membership be printed and a copy sent to each committee member. The total expense of such certificates to be limited to $25.00.

Council requested that Mr. Roddy, chairman of Preparatory and Post Tanning Committee, prepare in the proper format such methods of the "G" series as are necessary. These methods will be published. Such methods as can be found in any standard chemistry text are to be deleted.

Council in conforming to the By-Laws requests all committee chairmen to review the newly published methods (all of which are now provisional) and to recommend any which they and their committee feel should be dropped. Also they are to advise of any errors or corrections in the methods.

Dr. Flinn reported that the Physical Test Methods were now ready to be printed for the Methods Booklet. They are not to be republished in the Journal, but only for the Booklet.

Methods L-1 and H-10 are now ready in proper form for publication in the Journal and copies for the Booklet. Printers proofs will be sent to Messrs. Flinn, Maeser, Thorstensen and O'Flaherty.

The following letters have been assigned to the following series of methods.

"L" series is assigned to Biological Methods.

"N" series is assigned to Water Quality and Industrial Waste Disposal.

"M" series is assigned to a new series, Skin and Hide Evaluation. A committee is to be appointed to undertake work in this field.

Convention Committee report was made by Mr. D. Meo. The proposed budget of $3,900.00 was approved by Council.

The matter of registering all persons attending the meeting was discussed.

Tickets are to be provided for the Presidential Reception and the Banquet. Arrangements will be made with the hotel to sell banquet tickets to those who desire to attend but who are not registered at the hotel.

Council approved the use of the Association's public address system and the expenses of a person to operate it and the lantern. Such expense is not to exceed $200.00.

Mr. Meo suggested that the Association try to settle on three places and to rotate year to year at these same places. This would be subject to change if desired but as a beginning —

Mackinac Island	—	1956
Lake Placid	—	1957
Swampscott	—	1958

Council favors this as it is becoming increasingly difficult to find places where the full membership can be accommodated.

It was approved by Council that the registration will be $6.00 for members and $12.00 for non-members. For such persons who are from local tanneries and who wish to attend only one day's technical session a fee of $2.00 will be charged.

Editor Williams reported that he was concerned by the few papers he is receiving.

Mr. Wederbrand, reporting for the Ways and Means Committee, discussed the advertising schedule for 1955. It was agreed that Mr. Wederbrand would solicit the equipment companies.

The annual statement by Mr. Keck was approved and will be published in the Journal.

The budget for 1955 was discussed and approved. It is to be published in the Journal.

Mr. Telander reported that he had made arrangements to attend the International Union of Leather Trades Societies Meeting in Stockholm. Council charged him to represent the interest of the A.L.C.A. as his good judgement would dictate.

The committee on selecting the author of a paper for presentation at the International Union of Leather Trades Socieities Meeting reported that they had received three papers, anyone of which would justify the author being selected. After careful deliberation it was decided to accept the paper of Messrs. Kanagy and Robinson, "Studies on Leather by Means of a Sonic Technique". This is a new system of non-destructive technique being applied to leather.

Dr. Kanagy will present this paper. Council has approved the action of the committee, and Dr. Kanagy will be given $1,000.00 to help defray his expenses.

Council approved the slate presented by the Nominating Committee. This will appear in the February Journal.

A letter from Dr. Compton who was appointed to represent the A.L.C.A. at the Perkin Centennial was read. Dr. Compton is to organize a panel, and he is to have full authority to do this.

Council approved a membership card to be sent to each member who paid his dues. The Secretary is to have such cards printed and this card is to include the A.L.C.A. insignia.

The Awards Committee reported that they have not come to a final decision on the Alsop and Winheim Awards.

The following candidates were elected to Active membership by Council.

Eduardo Bernal	Chester E. Claff, Jr.	Raif Aljure Nasser
Johan Bjorksten	Lawrence B. Folsom	

The transfer from Associate to Active membership of Francis K. Keirnan was approved by Council.

The Secretary is to publish the number of members lost, the new members, and the net results.

The matter of having a committee in A.S.T.M. on Physical Testing was referred to Mr. Maeser, who is to report at the next meeting.

It was suggested that in the Presidential Message some reference be made to the privilege and responsibilities of members.

It was suggested that consideration be given to the appointment of a committee to review the By-Laws with the idea of streamlining them. This will be a matter of business at the next Council meeting.

Council approved a plan for the solicitation of members from the countries south of the United States. Lists of these tanners are to be furnished by Messrs. Meo and Wederbrand.

The Secretary is to prepare a letter and type it in both English and Spanish or Portuguese; then mail it to these tanners soliciting their membership.

Council expressed its appreciation for the hospitality of the Mead Corporation in making this meeting a very pleasant one.

The meeting was adjourned at 3:15 P.M.

Respectfully submitted,

FRED O'FLAHERTY, *Secretary*

FINANCIAL REPORT OF THE ASSOCIATION FOR THE YEAR ENDING DECEMBER 31, 1954

EXHIBIT "A"

COMPARATIVE BALANCE SHEET

DECEMBER 31, 1953 and DECEMBER 31, 1954

ASSETS

	1954	1953	Increase or (Decrease)
CASH			
Petty Cash on Hand	$ 2.28	$ 13.67	$ (11.39)
Cash in Bank	17,464.89	15,186.97	2,277.92
RECEIVABLES			
Accrued Interest Receivable on U. S. Treasury Bonds	62.50	62.50	–0–
A.L.C.A. Convention Fund Receivable	385.00	–0–	385.00
Accounts Receivable—Advertisers	1,827.65	2,538.40	(710.75)
Accounts Receivable—Reprints	228.75	155.10	73.65
Accounts Receivable—Directory	29.00	22.40	6.60
INVESTMENTS			
United States War Bonds Series "F", cost $2,960.00 plus accrued interest of $1,040.00 to December 31, 1954	4,000.00	7,848.00	(3,848.00)
United States Treasury Bonds 2½% due for redemption in 1972 but redeemable on and after June 15, 1967—Cost	13,000.00	13,000.00	–0–

United States Treasury Bonds 2½% Series "G" due in July of 1958 at cost	5,000.00	5,000.00	–0–
United States Treasury Bonds Series "F" cost, $3,700.00 plus accrued interest of $410.00 to December 31, 1954 due in November 1960 at par	4,110.00	3,985.00	125.00
United States Treasury Bonds 2½% due for redemption 1967 to 1972—Cost	4,839.06	4,839.06	
United States Treasury Bonds 2½% due for redemption 1967 to 1972—Cost	4,748.44	4,748.44	
United States Treasury Bonds 2½% due for redemption 1967 to 1972—Cost	4,910.94	–0–	4,910.94
United States Treasury Bonds 2½% due for redemption 1967 to 1972—Cost	996.56	–0–	996.56
Total Assets	$61,605.07	$57,399.54	$ 4,205.53

LIABILITIES

CURRENT LIABILITIES

Accounts Payable	$ 1,734.15	$ 1,763.38	$ (29.23)
Accrued Withholding Tax Liability	208.80	222.40	(13.60)

DEFERRED CREDITS TO INCOME

Dues Receivable in Advance	284.50	377.60	(93.10)
Subscriptions Received in Advance	3,001.76	2,757.14	244.62
Methods Received in Advance	–0–	3.40	(3.40)
Total Liabilities	$ 5,229.21	$ 5,123.92	$ 105.29

NET WORTH

Reserve for Foreign Meetings	$ 2,000.00	$ 1,000.00	$ 1,000.00
Surplus as per "Exhibit C"	54,375.86	51,275.62	3,100.24
Total Net Worth	$56,375.86	$52,275.62	$ 4,100.24
Total Liabilities and Net Worth	$61,605.07	$57,399.54	$ 4,205.53

EXHIBIT "B"

COMPARATIVE STATEMENT OF INCOME AND EXPENSE

YEARS ENDING DECEMBER 31, 1953 and DECEMBER 31, 1954

INCOME General	Year ended – December 31 1954	1953	Increase (Decrease)
Dues including Members' subscriptions to Journal (Net)	$10,753.50	$10,519.92	$ 233.58
By-Laws and Methods	289.04	–0–	289.04
Membership Booklets (Directory)	836.44	704.28	132.16
Interest on Government Bonds	1,108.52	1,064.27	44.25
Total	$12,987.50	$12,288.47	$ 699.03
JOURNAL (Exclusive of Membership Subscriptions)			
Advertising	$12,059.58	$12,147.00	$ (87.42)
Subscriptions—Non-Members	4,892.51	5,102.52	(210.01)
Journals, Bound and Unbound	615.62	749.90	(134.28)
Reprints	1,900.57	1,647.40	253.17
Dues, I.S.L.T.C.	995.00	814.00	181.00
Totals	20,463.28	20,460.82	2.46
TOTAL INCOME	$33,450.78	$32,749.29	$ 701.49

EXPENSE			
General			
Executive Secretary's Office Expense	$ 4,200.00	$ 3,999.84	$ 200.16
Secretary's Office Expense	879.91	1,020.31	(140.40)
Accounts Receivable (Dues) Written Off Uncollectible	229.90	389.00	(159.10)
Annual Meeting Expense	186.12	525.58	(339.46)
Auditing	150.00	125.00	25.00
By-Laws and Methods	2,859.17	–0–	2,859.17
Council Meeting Expense	69.15	142.91	(73.76)
Dues, International Leather	120.09	120.30	(.21)
Membership Booklets (Directory)	829.40	826.50	2.90
Winheim Memorial Award	–0–	200.00	(200.00)
Total	$ 9,523.74	$ 7,349.44	$ 2,174.30
JOURNAL			
Advertising Written Off—Uncollectible	–0–	$ 70.20	$ (70.20)
Committee Work	36.44	48.44	(12.00)
Editor's Compensation	1,000.00	900.00	100.00
Editor's Expense	591.44	565.18	26.26
Exchange on Foreign Checks	3.69	3.41	.28
Insurance Expense (Old Journals)	62.00	62.00	–0–
Journals	14,959.64	15,327.01	(367.37)
Miscellaneous Journal Expense (Counting, Binding, etc.)	116.50	99.00	17.50
Registered Copyrights	48.00	48.00	–0–
Reprints	2,222.61	2,094.35	128.26
Storage	300.00	350.00	(50.00)
Translations and Abstracts	350.20	428.53	(78.33)
Discount Allowed	136.28	115.30	20.98
Totals	$19,826.80	$20,111.42	$ (284.62)
TOTAL EXPENSE	$29,350.54	$27,460.86	$ 1,889.68

EXHIBIT "C"

COMPARATIVE STATEMENT OF SURPLUS
DECEMBER 31, 1953 and DECEMBER 31, 1954

	YEAR ENDED DECEMBER 31 1954	1953	Increase or (Decrease)
Reserve for Foreign Meetings at beginning of year	$ 1,000.00	$ –0–	$ 1,000.00
Add: Transfer from Surplus	1,000.00	1,000.00	–0–
Reserve for Foreign Meetings at end of year	$ 2,000.00	$ 1,000.00	$ 1,000.00
Surplus at the beginning of year	$51,275.62	$46,987.19	$ 4,288.43
ADD			
NET PROFIT			
General (Including Members' Subscriptions to Journal)	3,463.76	4,939.03	(1,475.27)
Journal (Excluding Members' Subscriptions to Journal)	636.48	349.40	287.08
DEDUCT			
Transfer to Reserve for Foreign Meetings	1,000.00	1,000.00	–0–
SURPLUS AT THE END OF YEAR	$54,375.86	$51,275.62	$ 3,100.24
SURPLUS AND RESERVE FOR FOREIGN MEETINGS AT END OF YEAR	$56,375.86	$52,275.62	$ 4,100.24

BUDGET FOR 1955

GENERAL ACCOUNT: INCOME	1954 Proposed	1954 Actual	1955 Proposed
Dues	$10,500.00	$10,753.50	$10,750.00
Interest on United States Bonds	1,000.00	1,108.52	1,100.00
By-Laws and Methods	–0–	289.04	500.00
Annual Meeting	–0–	–0–	–0–
Directory	850.00	836.44	850.00
Total	$12,350.00	$12,987.50	$13,200.00
GENERAL ACCOUNT: EXPENSE:			
Executive Secretary's Office Expense	$ 4,200.00	$ 4,200.00	$ 4,200.00
Secretary's Office Expense	1,100.00	879.91	1,000.00
Annual Meeting	200.00	186.12	200.00
Committee Work	100.00	36.44	100.00
Council Meeting	200.00	69.15	100.00
Auditing	125.00	150.00	150.00
Printing Methods and By-Laws	2,000.00	2,859.17	500.00
Printing Directory	900.00	829.40	850.00
Reserve for Uncollectible Accounts	500.00	229.90	300.00
Winheim Award	–0–	–0–	100.00
Total	$ 9,325.00	$ 9,440.09	$ 7,500.00
Surplus on General Accounts	$ 3,025.00	$ 3,547.41	$ 5,700.00
JOURNAL ACCOUNT: INCOME:			
Advertisements	$12,000.00	$12,059.58	$12,000.00
Subscriptions	5,100.00	4,892.51	5,000.00
Journals, Volumes, Reprints, Sold	1,500.00	2,516.19	2,000.00
Dues, S.L.T.C., Difference	800.00	995.00	950.00
Total	$19,400.00	$20,463.28	$19,950.00
JOURNAL ACCOUNT: EXPENSE:			
Printing and Publishing	$16,000.00	$14,959.64	$15,000.00
Printing Reprints	2,100.00	2,222.61	2,200.00
Copyright, Insurance, Storage	500.00	410.00	500.00
Abstracts and Translations	500.00	350.20	400.00
Editor's Salary	1,000.00	1,000.00	1,000.00
Editor's Office Expense	900.00	591.44	700.00
Advertising Discount Allowed	120.00	136.28	150.00
Total	$21,120.00	$19,670.17	$19,950.00
Difference on Journal Account	$ 1,720.00 (Deficit)	$ 793.11 (Surplus)	–0–
Surplus from General Account and Journal Account	$ 1,305.00	$ 4,340.52	$ 5,700.00

NECROLOGY FOR 1954

A. Cheshire (S.L.T.C. Member)
L. H. Lincoln
D. McCandlish
R. Paniker (S.L.T.C. Member)
Herman Richter
Swanie S. Rossander
Alex Saxe
Melvin Snider

SPECIFICATIONS FOR REAGENTS AND EQUIPMENT (H-10)

1. SCOPE

1.1 This method is intended to provide the specifications for desiccants, petroleum ether and thermometers used in the analysis of oils, greases and their products.

2. DESICCANTS

2.1 Sulfuric acid, sp. gr. 1.84. This is a satisfactory desiccant but must be maintained fairly fresh. It is very inconvenient, even hazardous, to handle.

2.2 Phosphoric anhydride powder. This is a satisfactory desiccant if a fresh surface is maintained within the desiccator. The concentrated phosphoric acid formed from the absorption of water is difficult to handle in unloading the desiccator.

2.3 Drierite, anhydrous calcium sulfate, 4 to 8 mesh. This is a satisfactory desiccant and may be obtained in the indicating variety which changes color from blue to red as water is absorbed.

2.4 Desicchlora, anhydrous barium perchlorate. This is a satisfactory desiccant.

2.5 Magnesium perchlorate, anhydrous. This is a satisfactory desiccant.

3. PETROLEUM ETHER

3.1 Specific gravity at 60°F. (15.5°C.), 0.630 to 0.660.

3.2 Color, water white.

3.3 Doctor test, sweet.

3.4 Saponification value, less than 1.0 mg. KOH per 100 ml. of petroleum ether.

3.5 Distillation test performed as directed in A.S.T.M. Designation 216-32.

a. Initial boiling temperature, not less than 35°C. and not over 38°C.

b. Dry flask end point, not less than 52°C. and not over 60°C.

c. At least 95% distilling under 54°C.

d. Not more than 60% distilling under 40°C.

e. Residue in distillation flask, neutral to methyl orange.

3.6 Copper strip corrosion test. Insert a small strip of polished copper in

the distillation flask containing petroleum ether. There should be no appreciable darkening of the copper during distillation.

3.7 Evaporation residue, 100 ml. of petroleum ether only, not over 0.0011 gram. Add 0.25 g. of stearin or similar hard fat (previously dried to constant weight at 101° ± 1°C.) to 250 ml. of petroleum ether. Evaporate the ether on a steam or water bath and dry the residue to constant weight at 101° ± 1°C. The increase in weight shall not exceed 0.003 g.

3.8 Unsaturated compounds, determined as directed on page 154 of the Analytical Edition of I. & E. C., March, 1938. A trace only is permitted.

3.9 Odor test. Immerse a strip of white unglazed blotting paper (1 inch x 4 inches x 0.166 inch) in petroleum ether for 30 seconds. Dry at room temperature in still air for 12 minutes. The paper should remain odorless.

3.10 Aromatic compounds. Add 5 drops of petroleum ether to 40 drops of H_2SO_4 (sp. gr. 1.84) and 10 drops of HNO_3 (sp. gr. 1.42) in a test tube. Warm for 10 minutes and then cool for 30 minutes. Transfer to a shallow dish and dilute with distilled water. There should be no nitrobenzene odor.

4. TITER TEST THERMOMETER

4.1 The following specifications are for thermometers used in titer test and melting point determinations.

Type: Etched stem glass.
Liquid: Mercury.
Filling above liquid: Evacuated or nitrogen gas.
Temperature range: −2° to +68°C.
Subdivisions: 0.2°C.
Total length: 385 to 390 mm.
Stem diameter: 6 to 7 mm.
Stem construction: Plain or lens front. The cross section of the lens front type shall be such that it will pass through an 8 mm. ring gauge but will not enter a 5 mm. slot gauge.
Bulb diameter: 5.5 mm. to not greater than that of stem.
Bulb length: 15 to 25 mm.
Bulb construction: Corning normal or equally suitable thermometric glass.
Distance from bottom of bulb to −2° mark: 50 to 60 mm.
Distance from 68° mark to top of thermometer: 20 to 35 mm.
Length of unchanged capillary between the highest graduation and the expansion chamber: 10 mm.
Expansion chamber: To permit heating to at least 85°C.
Top finish: Glass ring.
Longer graduation lines at each: 1° mark.

Graduations numbered at zero and each multiple of 2°.

Immersion: 45 mm., a line shall be etched around the stem 45 mm. from the bottom of the bulb.

Special marking on thermometer: A.O.C.S. Titer Test.

Maximum scale error permitted at any point: 0.2°C.

Marking on case: A.O.C.S. Titer Test, −2° to +68° in 0.2°C.

Standardization: The thermometer shall be standardized at the ice point and at intervals of approximately 20°C., for the condition of 45 mm. immersion, and for an average stem temperature of the emergent mercury column of 25°C.

5. CLOUD AND POUR TEST THERMOMETER

5.1 These specifications cover a special thermometer graduated in either Centigrade or Fahrenheit degrees as specified, the ranges being −38° to +50°C. or −36° to +120°F., respectively.

Type: Etched stem, glass.

Liquid: Mercury.

Range and Subdivision: −38° to +50°C. in 1°C. or −36° to +120°F. in 2°F.

Total length: 220 to 224 mm. (8.69 to 8.81 in.).

Stem: Plain front, enamel back, suitable thermometer tubing. Diameter, 7.0 to 8.0 mm. (0.28 to 0.31 in.).

Bulb: Corning normal or equally suitable thermometric glass.
Length, not over 9.5 mm. (0.37 in.).
Diameter, not greater than stem.

Distance to −38°C. or −36°F. line from bottom of bulb: 120 to 130 mm. (4.73 to 5.12 in.).

Distance to +49°C. or +120°F. line from top of thermometer: 19 to 25 mm. (0.75 to 0.98 in.).

Expansion chamber: To permit heating to 100°C. or 212°F.

Filling above mercury: Nitrogen gas.

Top finish: Plain.

Graduation: All lines, figures, and letters clear cut and distinct. Lines at multiples of 5°C. or 10°F. to be longer than the remaining lines. Graduations to be numbered at each multiple of 10°C. or 20°F.

Immersion: 108 mm. or 4.25 in. The words "108 mm. immersion" on Centigrade thermometers or "4.25 in. immersion" on Fahrenheit thermometers and a line around the stem 108.0 mm. or 4.25 in. above the bottom of the bulb shall be etched on the thermometer.

Special marking: "A.S.T.M. Cloud and Pour," a serial number and the manufacturer's name or trade mark shall be etched on the stem.

Scale error: The error at any point of the scale, when the thermometer is standardized as provided below, shall not exceed 0.5°C. or 1°F.

Standardization: The thermometer shall be standardized at the ice point and at intervals of approximately 20°C. or 40°F. for 108 mm. or 4.25 in. immersion and for an average temperature of 21°C. or 70°C. for the emergent mercury column.

Case: The thermometer shall be supplied in a suitable case on which shall appear the marking: "A.S.T.M. Cloud and Pour, -38° to +50°C." or "A.S.T.M. Cloud and Pour, -36° to +120°F." according to the type of thermometer.

Note:—For the purpose of interpreting these specifications the following definitions apply:

The total length is the over-all length of the finished instrument.

The diameter is that measured with a ring gage.

The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.

The top of the thermometer is the top of the finished instrument.

6. SPECIAL LOW CLOUD AND POUR TEST THERMOMETER

6.1 These specifications cover a special low cloud and pour test thermometer graduated in either Centrigrade or Fahrenheit degrees as specified, the ranges being -80° to +20°C. or -112° to +70F.

Type: Etched stem, glass.

Liquid: Toluene or other suitable liquid colored red with a permanent dye.

Range and subdivision: -60° to +20°C. in 1°C. or -70° to +70°F. in 2°F.

Total length: 227 to 231 mm. (8.92 to 9.08 in.).

Stem: Plain front, enamel back, suitable thermometer tubing. Diameter 7.0 to 8.0 mm. (0.28 to 0.31 in.).

Bulb: Corning normal or equally suitable thermometric glass.
Length, 8.0 to 9.5 mm. (0.31 to 0.37 in.).
Diameter, 5.0 to 6.5 mm. (0.22 to 0.26 in.).

Distance to -57°C. or -70°F. line from bottom of bulb: 120 to 130 mm. (4.73 to 5.12 in.).

Distance to +20°C. or +68F. line from top of thermometer: 35 to 45 mm. (1.38 to 1.77 in.).

Expansion chamber: To permit heating to +60°C. or +140°F.

Filling above liquid: Gas under pressure.

Top finish: Plain.

Graduation: All lines, figures and letters clear cut and distinct, lines at mul-

tiples of 5°C. or 10°F. to be longer than the remaining lines. Graduations to be numbered at each multiple of 10°C. or 20°F.

Immersion: 76 mm. (3 in.). The words "76 mm. immersion" on Centigrade thermometers, or "3 in. immersion" on Fahrenheit thermometers and a line around the stem 76 mm. (3 in.) above the bottom of the bulb, shall be etched on the thermometer.

Special marking: "A.S.T.M. Low Cloud and Pour," a serial number and the manufacturer's name or trade mark shall be etched on the thermometer.

Scale error: The error at any point of the scale when the thermometer is standardized as provided below, shall not exceed 1°C. or 2°F.

Standardization: The thermometer shall be standardized at the ice point and at intervals of approximately 20°C. or 35°F. for 76 mm. or 3 in. immersion, and for an average temperature of 21°C. or 70°F. for the emergent liquid column.

Case: The thermometer shall be supplied in a suitable case on which shall appear the marking "A.S.T.M. Low Cloud and Pour, –80 to +20°C." or "A.S.T.M. Low Cloud and Pour, –112 to +70°F.," according to the type of thermometer.

Note: For the purpose of interpreting these specifications, the following definitions apply:

The total length is the overall length of the finished instrument.

The diameter is that measured with a ring gage.

The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.

The top of the thermometer is the top of the finished instrument.

ALCA Provisional Method, January 1955

THE RESISTANCE OF LEATHER TO THE GROWTH OF FUNGI

(L1)

1. SCOPE

1.1 This method is used to evaluate the resistance of any leather to the growth of fungi or molds: it is applicable to untreated leathers as well as those containing agents to promote fungi resistance.

2. SPECIMEN

2.1 The specimens shall consist of two squares of leather each approximate-

ly two by two inches cut from each test unit of leather required in Method J1, Part 1.

2.2 The specimens shall be taken adjacent to test area W of Method J1, Part 1. If the test unit does not contain this area, the specimens shall be taken from a representative test area.

2.3 Control specimens shall consist of four squares of leather, each approximately two by two inches, cut from leather known to be untreated and similar in type and tannage to the leather under test. Separate sets of four squares shall be used for each alternate procedure in Section 4 below.

3. INOCULUM AND APPARATUS

3.1 Inoculum—The inoculum shall consist of a mixture of fungi spores on sand. This inoculum is furnished by the Tanners' Council Research Laboratory, University of Cincinnati, Cincinnati 21, Ohio. The inoculum mixture shall be accompanied, when received, by a specification sheet stating the species of fungi included and its viability expiration date. The viability within this period shall be preserved by storage in a cool, dry, darkened area.

3.2 Apparatus capable of drumming the test squares with distilled water as required in Section 4 below.

3.3 An incubation chamber in which a temperature of 29°C. ± 2°C. and a relative humidity greater than 85% R. H. can be maintained. A sealed glass bottle containing water in its bottom and placed in a 29°C. oven or room will provide the necessary humidity and the separate incubation chambers required in Section 4 below.

4. PROCEDURE

4.1 *Method A.* Resistance where leaching of the active agent is not concerned.

4.1.1 One square of leather from each test specimen set from each test unit shall be immersed in distilled water at 23±5°C. for five to ten minutes. The different groups of squares from different samples shall be immersed separately, but all squares from the same leather sample should be immersed together in a minimum quantity of water to cover them. The squares shall be removed, drained and blotted. The moist leather shall be immediately inoculated, either by dusting the spore-sand mixture onto the leather surfaces or by painting a spore suspension onto all surfaces of the squares. This suspension is made by shaking ten gram of the sand-spore mixture with 100 ml. of distilled water, and decanting the spore suspension from the sand.

The inoculated squares are hung on a glass rod inserted through a hole in one side of the squares, suspending them so that they touch no other surface,

all squares from a single leather being placed on a single rod. This pack of leather squares is incubated at 29 ± 2°C. and better than 85% R. H. for at least 30 days. Each different leather shall be incubated in a separate compartment to prevent any volatile active agents from causing interfering results. The incubating samples shall be inspected at least weekly to determine, by visual means, any mold growth. If the incubation chamber is a closed glass container, each inspection shall involve opening and ventilating the jar briefly to dissipate any volatile active agents and to allow free access of air.

4.2 *Method B.* Resistance after leaching to remove soluble actives. Method B uses a second square of leather from each test specimen set from each test unit. The several squares from a given leather sample shall be combined, weighed and drummed for three hours with 30 times their weight of distilled water at 23 ± 5°C. to leach readily soluble materials from the leather. The leached squares shall be removed, drained, blotted, inoculated and incubated as the squares in Method A, Section 4.1.1 were.

4.3 The sets consisting of four control squares shall be treated similarly to Method 4.1 and similarly to Method 4.2. These squares should develop mold growth in the fashion characteristic for the particular type of untreated leather; if all the control squares do not mold, the test leather squares shall be discarded and the test repeated.

5. RESULTS

5.1 If none of the leather squares in a given sample show visible mold growth after 30 days in both methods A and B, while both control sets have molded, the leather may be described as "very mold resistant".

5.2 Whenever the leather being tested shows some mold growth, the report shall include the extent of growth (slight, moderate and heavy) and the time for the first appearance of growth, as well as the Method (A or B) used. Slight growth shall describe isolated areas of growth on the squares, while heavy growth shall describe complete coverage of the surfaces of the squares.

6. HISTORY AND STATUS

6.1 This method was adopted as a provisional method in 1946, and became official in 1949. The development of the method has been critically considered by Cordon (Journal of American Leather Chemists Association **42**, 302-312 (1947).

ALCA Provisional Method, January 1955.

Resistance of White Leather to Breakdown by Perspiration

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INTRODUCTION

The breakdown of chrome tanned white shoe upper leather due to perspiration is a problem that occasionally causes concern to the shoe manufacturer and to the tanner. To study the nature of the constituents of perspiration which are most likely responsible for the rapid deterioration which occurs, white shoes showing various degrees of damage were submitted to us by a tanner. Considerable testing and analyses had been conducted by the tanner on this problem and we were furnished with a complete set of data on the tests and analyses which had been conducted. This formed the basis for this research.

Colin-Russ [3] had made an extensive study of the composition of perspiration and proposed a composition for artificial perspiration based on his experience with the deterioration which occurred in chrome tanned upper leather. He found that hydroxy acids were important constituents in gradually detanning full chrome uppers. For this reason he included lactic acid in the synthetic perspiration he used.

Colin-Russ had postulated a mechanism of detannage of chrome tanned shoe upper leather which indicated that lactic acid will detan and ultimately convert chrome leather to slimy particles. He also reported urea will induce a gelatinous, powdery and brittle state and salt embrittles the leather. The constituents of perspiration cause an alteration in the basic chrome complex, resulting in a less stable compound which can be washed out of the leather by excessive perspiration or water. Lollar [6] found that with acid dechroming agents, organic acids were more effective than inorganic acids. Any acid which ionizes to give an appreciable ion concentration will dechrome, either due to its acid reaction or penetration of the negative ion into the chrome complex to form stable, soluble compounds with the chromium.

EXPERIMENTAL

Figure I shows two badly damaged shoes. In the vamp the leather has cracked completely through in the area directly over the little toe. Right in

*Presented at the 50th Annual Meeting of A.L.C.A., Bedford Springs, Pa., June, 1954.

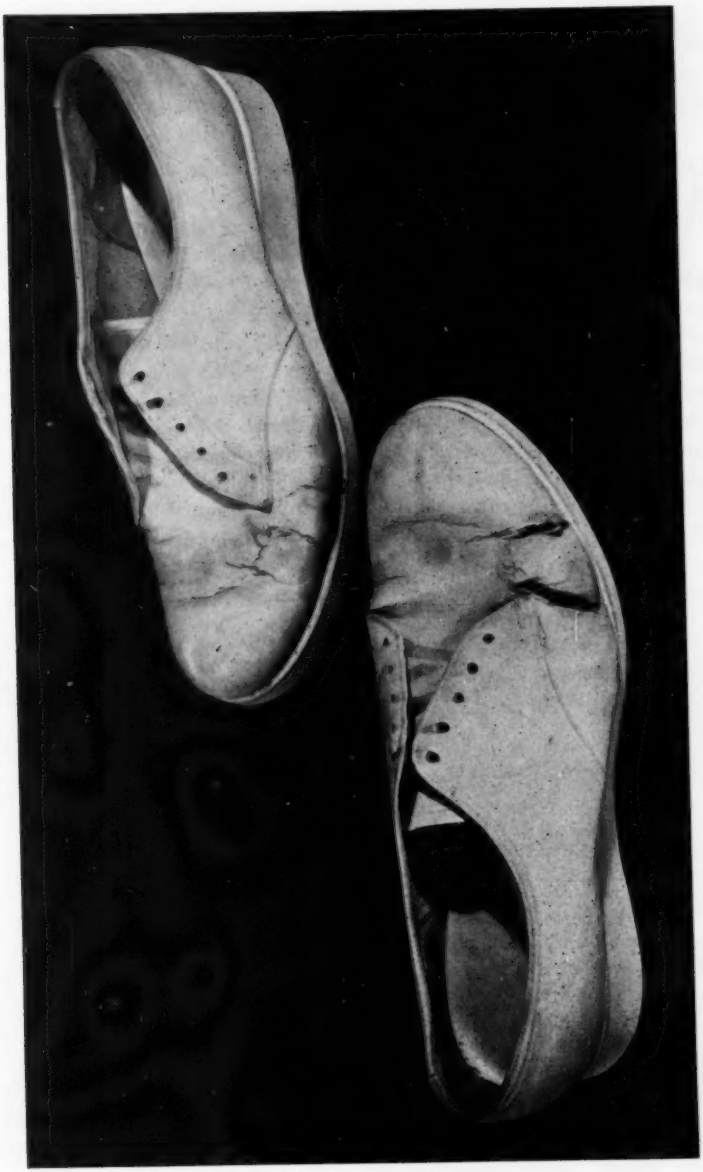


FIGURE 1—Damaged white shoes showing cracks and discoloration caused by excessive perspiration.

back of this region is a spot which shows the chrome discoloration where the leather is beginning to harden and chrome has migrated from the fibers in such areas. The surface of the leather in the damaged areas range in color from green in the slightly damaged areas to a violet color in the badly damaged areas.

Chemical analyses of the damaged areas of worn white shoes in some cases showed less grease than the undamaged areas of the same shoes but in many cases the difference was so slight as to be negligible. It is possible that some of the fat from the fatliquor originally used to lubricate the leather is lost during wear but the oil from the skin of the wearer may replace it.

In analyzing the good and the damaged areas of worn white shoes a significant difference was observed in the tryptic digestibility of the two areas as shown in Table I. When undamaged and damaged areas were subjected to tryptic digestion [7] the damaged areas showed an increase in soluble solids and in nitrogen. Using the hydroxyproline assay [8] as an index of collagen which was digested, as much as 26 to 28 percent collagen was solubilized by trypsin in the damaged areas, while less than ten per cent collagen solubilization was observed in undamaged-worn areas and none in the original leather.

TABLE I

Tryptic Hydrolysis of White Leathers and Chrome Leather in the Blue
Per Cent Solubilized—Correcte l for Solids of Enzyme Solution

Leather	Inactivated	Activated
Shoe 4 Undamaged Area	7.70	17.80
Shoe 4 Damaged Area	26.95	67.00
Shoe 7 Undamaged Area	7.65	24.95
Shoe 7 Damaged Area	29.75	65.05
Full Grain Elk	4.90	36.15
Corrected Grain	8.00	19.10
Corrected Grain Buck	5.20	21.80
Chrome in Blue	1.80	3.05

The damaged areas of the shoes showed a higher water soluble chrome than the undamaged areas. In very badly damaged areas as much as 10 per cent of the chrome was converted to a soluble form. To obtain the soluble chrome one gram of leather was boiled in 50 mls. of water for two hours and the total chrome determined on the extracts.

While some of the chrome is soluble in the damaged areas it is still in the trivalent form. However, some of the chrome ash from the badly damaged areas of the shoes had a distinct yellow color indicating that this chrome had been altered by the perspiration, changing from trivalent form to hexavalent during the ashing. This same condition was observed by the cooperating tanner on badly damaged shoes.

The yellow ash is water soluble and can be separated from the remaining insoluble ash. From the vamp of one damaged shoe approximately half of the total chrome present was as a soluble ash while the other half was insoluble in water. This yellow ash is obtained when sodium lactate is added to the original leather and the treated leather is ashed.

As Colin-Russ [2] found that hydroxy acids gradually detanned chrome upper leather, the worn white shoes and leather received from a tannery were analyzed for lactic acid content. A colorimetric method was used to determine lactic acid content of the leathers and the results are given in Figure 3. This method depends on the sulfuric acid conversion of lactic acid to acetaldehyde and the estimation of the formed acetaldehyde by measuring the color produced with para-hydroxy-diphenyl in the presence of copper ions. [1] The method will not distinguish lactic acid from certain other hydroxy acids and acetaldehyde. Formaldehyde gives a similar color, but this could be distinguished with the Beckman spectrophotometer.

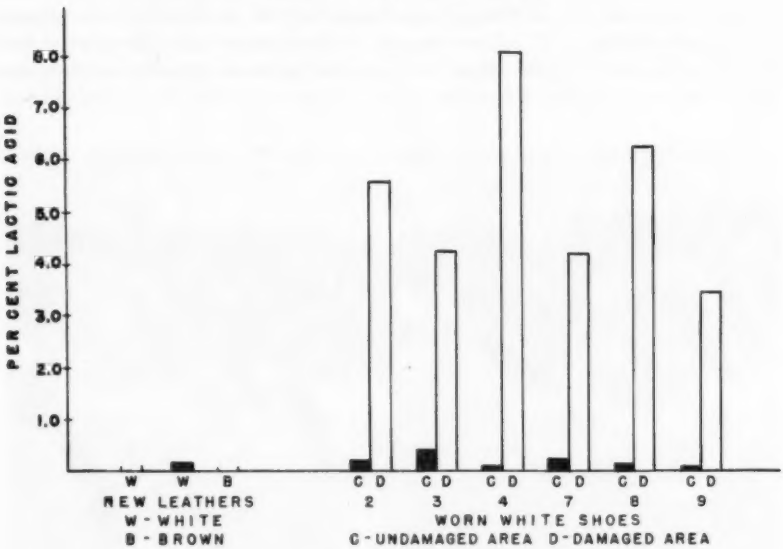
Cross sections made of the damaged areas appear as shown in the photomicrograph in Figure II. Examination of the cross-section shows that the chrome migrates from the fibers and appears as loose particles in the interspaces between the fibers directly under the grain surface. It is this altered

FIGURE II—Photomicrograph of a cross-section made from a badly damaged area of a white shoe. Chrome has migrated from the fibers into the interspaces directly below the grain surface to cause a discoloration.

chrome which appears yellow in color when micro-incinerated cross-sections are made to demonstrate the ash pattern.

The results given in Figure III show that the new leathers secured from the tannery had very little lactic acid present. The counter area from the worn white shoes which showed no perspiration damage had little lactic acid present. However the damaged areas from the shoes showed a considerable amount of lactates expressed as lactic acid present in each case. The results also indicate that variable amounts of lactate occur in human perspiration. Some individuals may have a much greater concentration of this component present in their perspiration than others and the damaged shoes show that the greater the concentration the greater and more rapid the damage.

FIGURE 3
LACTIC ACID CONTENT OF
NEW AND WORN LEATHERS



Perspiration Tests

To obtain some method of predicting the resistance of white leathers to perspiration several testing procedures were tried. Because the discoloration, stiffening and cracking of the white leather shoes occurred to the greatest extent in the vamp area it was felt that flexing the leather while in contact with synthetic perspiration would duplicate the damage.

Specimens of white leather were flexed on the Hopton dynamic flex tester with the application of artificial perspiration while flexing at room temperature and then drying in an oven at 40°C. overnight. The artificial perspiration was that given in KK-L-311,[5] buffered to a pH of 7. The wetting and drying cycle was repeated for several weeks but only limited breakdown occurred and based on subsequent data indicates that flexing plays only a minor role in deterioration. Furthermore, in all of the damaged worn shoes even in the vamp area the damage very often had its starting point at pressure spots such as produced by corns and other foot defects.

As the cross-sections of the leather from badly damaged areas of the shoes showed that the chrome had migrated to the outer perimeter of the damaged area a procedure to simulate this migrating action was tried. The cooperating tanner had observed a considerable increase in sodium chloride content in the damaged areas of worn white shoes. By dropping repeatly onto leather and allowing it to dry solutions of sodium chloride, sodium lactate or sodium butyrate, migration of the chrome occurred and each solution stripped chrome from the leather fibers.

The cooperating tanner had previously observed the same effect when he allowed synthetic perspiration to fall dropwise on the white leather when placed on a steam bath. The chrome migrated from the center of the spot where it was in contact with the perspiration to the outer edges away from the steam bath where the migrated chrome and perspiration salts crusted and dried.

The sodium lactate and the sodium butyrate were much more active in causing migration of the chrome from the fibers than the sodium chloride. Urea is found in perspiration and when a solution of urea was allowed to drop on the chrome leathers it had but little effect.

To duplicate the accumulated effect of perspiration in the leather, samples were soaked in the synthetic perspiration given in KK-L-311 buffered to pH of 7, and held in sealed jars above a water level to insure a saturated humidity at temperatures of 50°C., 60°C., and 70°C. After two days the samples were removed and examined for breakdown. The greatest breakdown occurred at 70°C. and using this procedure it was possible to obtain considerable grain crack strength reduction in some of the white leathers.

A shoe manufacturer submitted seven sides of white leathers representing tannages from seven tanners. Specimens from these sides were tested using the synthetic perspiration of KK-L-311 and were held in sealed jars at 100 per cent relative humidity and at 70°C. for two days. The specimens showed variable breakdown and seemed to be related to the experience of the shoe manufacturer with the serviceability obtained in shoes. Those tannages showing little change in strength and no shrinkage during test were found by

the shoe manufacturer from wear experience to be the best. Those showing considerable breakdown, cracking when wet and shrinking as much as 50 per cent when dried, are no longer used by the shoe manufacturer because they failed in actual service.

Chemical analyses of the seven sides of leathers showed variable percentages of chrome. When shrinkage temperature was determined on these leathers all were below the boiling point of water, ranging from a low of 80°C. to a high of 97°C. The chrome content ranged from 1.39 per cent to 3.27 per cent of the moisture free basis. There was no direct relationship between resistance to deterioration and chrome content or shrinkage temperature.

While the KK-L-311 synthetic perspiration gave breakdown similar to the shoe manufacturer's experience the appearance of the leather was not the same as that in worn shoes. As sodium lactate treatment gave the discoloration and chrome migration in worn shoes, sodium lactate was added to the Colin-Russ synthetic perspiration mixture so as to have a concentration of 5 per cent and the pH was adjusted to 7.5. The sodium lactate was used rather than lactic acid because it was thought that it would be in the worn leather as a salt.

Specimens of white leather were wetted in this perspiration mixture until completely saturated and were then suspended above a water level at 70°C. for two days. The tannages showed the same pattern of breakdown as obtained with the KK-L-311 synthetic perspiration except the action was more drastic and discoloration of the leather occurred.

Tanners of white side leather were informed of the problem and nine tanners submitted sides for test purposes. Eleven sides were received. When tested using the sodium lactate modified Colin-Russ synthetic perspiration variable breakdown occurred on the leathers. Some tannages showed little breakdown while others were badly damaged. To obtain a more precise indication of the degree of change in the leathers after perspiration test the grain crack strength was determined on the specimens before and after treatment and the results in Table II were obtained.

Examination of the data shows some of the leathers have considerable reduction in grain crack strength while others showed only slight differences. Elk sides 1, 2, and 6 show considerable reduction in strength. Also apparent is the difference in initial grain crack strength of the eleven sides represented. With only one side tested in each case, the variation could be in the sides as well as due to different tannages.

To obtain the variation in grain crack strength which occurred from side to side of the same tannage within a small area, pieces from the same area of twelve sides were used. These pieces were supplied by a tanner interested in the problem. From each piece four specimens were cut for the test. Two were

TABLE II

Resistance of White Leathers to Breakdown by Perspiration
Grain Crack Strength (lbs.) Before and After Perspiration Treatment

Elk Side 1	Control	Aged	Elk Side 2	Control	Aged	Elk Side 3	Control	Aged	Elk Side 4	Control	Aged
1	605	35	1	325	25	1	370	305	1	540	330
2	575	25	2	240	30	2	390	400	2	425	230
3	580	40	3	370	25	3	490	315	3	385	200
Ave.	587	33	Ave.	312	27	Ave.	417	340	Ave.	450	253

Elk Side 5	Control	Aged	Elk Side 6	Control	Aged	Elk Side 7	Control	Aged	Elk Side 8	Control	Aged
1	580	230	1	570	95	1	280	235	1	800	250
2	315	240	2	550	55	2	270	190	2	790	390
3	440	240	3	610	180	3	290	235	3	770	330
Ave	445	237	Ave.	577	110	Ave.	280	220	Ave.	787	323

Kip Side 1	Control	Aged	Kip Side 2	Control	Aged	Kip Side 3	Control	Aged
1	800	630	1	450	320	1	430	485
2	850	585	2	400	340	2	575	440
3	860	505	3	460	370	3	495	305
Ave.	837	573	Ave.	437	343	Ave.	500	410

TABLE III

Resistance of Twelve Sides of White Leather to Breakdown by Perspiration
as Representative of One Tannage.
Grain Crack Strength (lbs.) Before and After Perspiration Treatment.

		Control	Aged			Control	Aged
Side	1			Side	7		
	1	500	560		1	480	360
	2	800	570		2	590	425
Side	2			Side	8		
	1	345	440		1	545	400
	2	665	300		2	745	430
Side	3			Side	9		
	1	780	480		1	520	235
	2	790	480		2	345	330
Side	4			Side	10		
	1	455	370		1	640	480
	2	550	310		2	570	550
Side	5			Side	11		
	1	455	290		1	480	395
	2	465	420		2	440	400
Side	6			Side	12		
	1	320	380		1	660	440
	2	500	440		2	570	500

subjected to the perspiration test and two were tested as received. The results are given in Table III. Examination of the data shows that the specimens subjected to the aging test have decreased in strength in almost all cases. Also there was a variation in grain crack strength from side to side on the leathers as received. An analysis of variance showed a very significant difference between the control samples and the treated samples. There was also a significant difference in the samples from side to side.

Other Chrome Tannages

The detanning of chrome tanned leather by perspiration is most readily noticed in white shoes. As these shoes are not lined in most cases the leather comes directly in contact with the perspiration. However, a pair of men's shoes, (brown in color) which were cloth lined, showed the same characteristic cracking in the vamp as observed in the white shoes. An analysis of the leather of these shoes revealed a high lactic acid content in the damaged area and almost two thirds of the chrome was present as a soluble ash. Therefore the problem of perspiration breakdown is not limited to chrome leathers finished as whites but will occur in other chrome tanages. The higher initial chrome content of the leathers going into tan and black colored leathers affords more protection than in the case of whites but they show the same mechanism of breakdown. This would agree with the results of Colin-Russ [2] and of Gallay and Tapp [4].

Summary

Perspiration causes a detannage of chrome leather and acts upon the detanned collagen to give rapid breakdown. Analytical results to determine the alteration of the hide substance in worn white shoes and other chrome leathers are given.

The change in the basic chrome tannage effected by components of perspiration has been reviewed. The hydroxy acid components of perspiration are capable of causing change in the chrome in the leather and leave the fibers in an unprotected condition.

Addition of sodium lactate to synthetic perspiration is necessary to obtain all the effects observed in badly damaged shoes including discoloration. The leathers treated with synthetic perspiration containing sodium lactate when subjected to a temperature of 70°C. at 100 per cent relative humidity for two days show varying degrees of breakdown. Lower temperatures cause a lesser breakdown but extension of the time period gives the same effect as obtained at 70°C.

Acknowledgments

The data and damaged shoes from the cooperating tanner and damaged shoes from the shoe manufacturers are gratefully acknowledged. Miss Helen Steinle and Mrs. Jean Tancous have performed a portion of the analyses, and their assistance has been important in the completion of this study.

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Received Oct. 19, 1954.

Discussion

Alfred G. Fleisch (Pfister and Vogel Tanning Company): First of all, we should thank Bob for getting down to some essentials of why we are getting breakdowns in leather. I am sure all of us in the tanning industry have had these complaints come to us and wondered why they had happened.

I am also sure there will be quite a few questions from the floor. But before we do open the discussion to the floor, I would like to ask Bob if he tried the lactic acid perspiration test on brown leathers and what the results were.

R. M. Lollar: W. T. Roddy has worked on that and is more familiar with it than I am.

Roddy: We have tried it on some brown and black chrome tanned calf and kid and some side leather. One point was not brought out in the talk: That in all cases the white leathers which we tested had a shrinkage temperature below the boil point, whereas in the case of the browns and black which we tested by the accelerated aging test the shrinkage temperature was above, but there was a decrease in strength.

Lollar: It is my feeling that there will be a reasonable degree of correlation between shrinkage temperature and deterioration as observed in this test, and also between this tryptic digestability and the deterioration as observed

in this test. You will notice that the white leather tryptic solubilities were higher than the chrome in the blue. For most of the stable tanned leathers the blue results would be more typical than the white results.

GEORGE E. BEST (Mutual Chemical Company of America): You mentioned, Dr. Lollar, that you noted chromate chromium—hexavalent chromium—in the ash from these leathers. You are not suggesting that the chromate chromium forms prior to the ashing, are you?

LOLLAR: No. We are not. We can see no trace of the yellow shade in the cross sections and we do find that the yellow shade and the material which reacts as hexavalent chromium shows up after the ashing procedure. We believe that oxidation occurs during the ashing procedure and as I indicated in the talk we have been able to add lactates to leather which we know contains no dichromate and after the ashing we find the dichromate present. It occurs during the ashing procedure. I believe it is an oxidation much like that which would occur in the actual oxidation of an ore, where the air is the oxidizing agent.

BEST: Simply heating chromic oxide in the air without addition of alkali will produce a certain amount of hexavalent chromium. If alkali were used you might expect oxidation to occur to a greater extent.

LOLLAR: While large concentrations of sodium chloride would produce some of this, large concentrations of sodium lactate would more likely produce the effect, and it is that that we are actually adding to the perspiration. There is another problem of the use of lactic acid directly and that is, that lactic acid in concentrated solution forms inner anhydrides which, unless you carefully break them down, do not give the monomer of lactic acid; this is another reason for using sodium lactate to avoid the complication of the variation in the actual acidity of the solution if we started from lactic acid.

FRED O'FLAHERTY (Tanners' Council Research Laboratory): This is a question that I know interests us all and you may wonder how it happens that the lactates get into the leather because everybody does not have lactates in their perspiration.

We have had this experience, that one person at least who had their physician prescribe for them calcium lactate to be taken to supply the calcium lacking in their system, found when they were taking calcium lactate, they developed shoe trouble which they never had before.

Then we have heard since that time, and have not been able to substantiate it, that in some of the foot powders that are being sold, a certain amount of calcium lactate is incorporated as a vehicle for the other ingredients put in there. So that would, in one way, account for the fact that not everybody is hard on white shoes. There are some persons who have worn them

for many years and have had no trouble; the same leather being produced and put in another pair of shoes goes very rapidly. So there is that point in understanding the mechanism that should be taken into consideration.

S. Hoover: Is this a phenomenon of ladies' shoes?

Lollar: No. It just happens that most of the shoes we have examined have been from nurses shoes.

S. S. Kremen: Do you think that any of the materials which are specifically used in white shoe leather manufacture such as syntans and pigments have any influence to giving it a greater predisposition to deterioration?

Lollar: I suspect so. I am not yet able to identify the mechanism of why that is true. As Bill Roddy mentioned, we do know most of these white leathers had a lower shrinkage temperature and that is correlated, certainly. You may recall work Pierce did when working with me as a graduate student, indicating lowering of the shrinkage temperature of chrome tanned leather by concomitant use of syntans. There may be a relationship there. I am not willing to say yet that that is necessarily true but it seems suggestive to me.

Fleisch: Are there further questions?

Malcolm H. Battles (A. C. Lawrence Leather Company): Dr. Lollar, as you are aware, the retanning of chrome upper leather uses quantities of ligno-sulfonate and in some of these there is present lactic acid. What effect would you predict in using ligno-sulfonic acid containing lactic acid in a retanned leather?

Lollar: I see no reason to assume that the source of the lactic acid, or the lactate will have any difference in its effect on the chrome complex ion. Since I visualize that this effect is probably a penetration of the chrome complex by the lactic acid, driving the carboxyl groups of the protein out of the complex, I would assume that any time when lactates are added to the leather in sufficient quantity that there will be this detannage.

I emphasized in the presentation that the lactic acid was present in an amount as great or greater than that of the chromium and I think that is a significant portion of the situation. If you have that situation, I believe that you will expect to get some of this action upon the chrome salt.

C. W. Mann: You not only can expect to—you do get the same type of deterioration in retan leather. In studying this problem on Army retanned upper leathers at the present time we find that there generally is a very high ash content in the deteriorated leathers, usually on the order of 8 to 10 per cent. The same type of degradation and cracking which you illustrated here frequently occurs in Army shoes after only a short time of wear. Many

times cracks appear after less than one month of wear. We do not know yet what causes it or how to prevent it, but we are studying the problem.

We do find, as you have found, that there is a high ash content in the damaged leather, but we generally have not found anything unusual about the pH of the leather, the chrome content, or the composition in different layers of the leather. The composition of the deteriorated leather seems to fall within the normal pattern with respect to those characteristics. However the lactic acid problem may have a bearing on it and we will go into that.

LOLLAR: I should like to reemphasize that the significant difference we have observed in these analyses—and we performed many more I did not even hint at, to try to get these leads—is this very high content of lactate in these leathers and I do believe, in these leathers at least, (but I do not attempt to generalize for all deteriorations) that the effect of lactate on the chrome complex was the cause of the deterioration.

PAUL L. BERNHARDT (Rohm and Haas Company): Do you feel there is a bacterial action that takes place along with this lactic acid condition in the light leathers?

LOLLAR: Chrome tanned leather is natively too acid for any great amount of bacterial growth to occur on it. We have conducted some independent experiments on the effect of the growth of molds on leather and do not find that the mold growth, per se, has directly an influence upon the stability of the tannage. To the extent that the microbic growth would produce organic acids, and many microbes do product such acids, there might be an indirect effect. But directly the chrome protein complex is fairly resistant to the action of the growth of the micro-organisms. The growth occurs on other substances such as the grease and finish materials, long before it occurs on the chrome protein complex.

Mechanism of Unhairing Skins and Hides by Means of Certain Proteolytic or Amylolytic Enzymes

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A good deal of work [1] has been done on the application of proteolytic enzymes to dehairing skins and hides. It is generally accepted [2] that the oldest process of unhairing viz., the "sweating" process depends on the action of bacterial enzymes. In the traditional liming process also, enzymes may be

secreted [2] from the bacteria present in the old lime liquor. It is still a much debated problem as to whether the enzymes derived from bacteria present in the old lime liquor are responsible for the unhairing. The first successful enzymes unhairing was achieved in 1910 by Röhm [3] who patented the process known as "Arazym process" in which pancreatic enzymes were used. The use of pancreatin [4], cathepsin [5] or the enzymes present in fish entrails [6] for unhairing was also reported. A series of patents are available on enzymic unhairing by the application of proteolytic enzymes derived from certain molds e. g. *P. glaucum* [7], *Mucor mucedo* [7], *A. niger* [7], *A. oryzae* [8], *A. flavus* [9], *A. parasiticus* [10], as well as from certain proteolytic bacteria like *B. mycoides* [11], *B. megatherium* [12], *B. mesentericus* [11, 13], *B. subtilis* [11, 13], *B. liquifacius* [13], *B. sphaericus* [14], *and B. vulgatus* [14]. The use of proteolytic enzymes prepared from certain molds in wool loosening of sheepskins has also been reported [15]. Recently, it has been shown [16] that unhairing by means of certain mucolytic enzymes viz., diastase, pectinase, pancreatic elastase is also quite practicable. The only plant protease the use of which was patented [17] for unhairing is papain.

By the use of the latex of madar plants (*Calotropis gigantea*), a new process of unhairing skins and hides has been developed by the authors [18] for the production of different types of leather. It has also been demonstrated that the proteolytic enzyme present in the latex is mainly responsible for its unhairing action. Another new process of enzymic unhairing making use of mucolytic enzymes viz., amylase prepared from a cheap cereal "ragi" (*Eleusine Coracana*) has been developed by the authors [19] for the production of different types of leather. The exact mechanism of unhairing action of proteolytic enzymes is not yet known. The subject has been all the more complicated because of the finding [16] that carbohydrate splitting enzymes like diastase are also equally capable of unhairing skins and hides. It was, therefore, of great interest to study the mechanism of the new processes of enzymic unhairing. With a view to demonstrate the mechanism of enzymic unhairing by these processes, the important skin proteins of both fibrous and non-fibrous type viz., collagen, reticulin, elastin, keratin, albumin, globulin and glycoprotein (mucoids) were individually prepared from skins or hides and the action of the protease isolated from madar latex was studied under controlled conditions on the individual proteins. The action of diastase or amylase of "ragi" was also studied on the mucoids of skins.

Experimental

Standard methods of preparation of the individual skin proteins were followed with such of the modifications as were found to be more useful and practicable. A brief outline of the modified method of preparation of each protein is described below:-

Collagen[20]:

The hair from a piece of fresh buffalo-hide was shaved off with a razor. The piece was drummed with 10 per cent sodium chloride solution and washed well with water to remove some of the globular proteins. It was then dehydrated in acetone and the whole epidermal layer up to the upper part of corium major was removed in a splitting machine so as to get rid of any keratinous protein and the bulk of the elastin fibres which were deposited in the upper part of the corium. From the flesh side also, the outer layers were similarly removed so as to obtain the corium major which was then cut into very small pieces. The material was then subjected to tryptic digestion in three changes of aqueous tryptic medium under properly controlled conditions and thoroughly washed to remove the remaining elastin and globular proteins which were hydrolysed by trypsin. It was then dehydrated in alcohol, air dried and finely ground in a Wiley mill. The ground material was extracted with acetone and then with alcohol to remove the lipids. The solvent extracted material was air dried and extracted with half-saturated calcium hydroxide solution in a mechanical shaker to remove the mucoid materials. The process was repeated at least three times till the extract was free of mucoids. The powder was then washed repeatedly with cold very dilute solution of acetic acid and then with cold distilled water. The collagen was finally dehydrated in alcohol, treated with ether, air-dried and reground in a Wiley mill.

Reticulin[21]:

A fresh calf skin was unhaired by the liming process and washed well with water. The unhaired pelt was dehydrated in acetone, cut into small pieces and subjected to tryptic digestion under properly controlled conditions in order to remove elastin and the remaining globular proteins. The pieces were thoroughly washed with water and extracted first with acetone and then with alcohol to remove the fat. To hydrolyse and to remove collagen, the fat-free material was boiled in two changes of 0.05 *N* caustic soda, for about two hours in each and the residue which consisted of very thin delicate films of reticulin tissue was then boiled with water and washed with warm water. It was then dehydrated in acetone and finely ground in a Wiley mill.

Elastin[22]:

The *ligamentum nuchae* was isolated from the neck of a cow and was obtained fresh from the slaughter house. The material was freed of any extraneous tissue and cut into thin strips.

It was extracted with dilute sodium chloride solution and thoroughly washed to remove all albumins and globulins. It was then extracted repeatedly with boiling water to remove collagen, and then with dilute potassium

hydroxide solution, followed by water and dilute acetic acid. After treating with cold dilute hydrochloric acid solution and washing thoroughly in water, it was finally extracted with hot alcohol and ether, air dried and finely ground in a Wiley Mill.

Keratin[28]:

The wool from a fresh sheep skin was clipped off with a scissor, washed well, air-dried and finely powdered. The powder was extracted with alcohol and then with ether to remove fats. It was then subjected to digestion with an acid pepsin solution, followed by an alkaline trypsin solution. Both digestions were carried out under properly controlled conditions. The keratin was re-extracted with alcohol and with ether and air-dried.

Albumin:

A goat skin obtained fresh from the slaughter house was freed of any blood and flesh and the hair was shaved off with a razor. The skin was chopped into small pieces and minced into a pulp in a meat mincer. The pulp was extracted with water in a mechanical shaker. Albumin was recovered from the water extract by distillation under high vacuum at 28 °C and finally by drying the residue in a vacuum desiccator.

Globulin:

The minced material was repeatedly washed with water to remove any remaining albumin and then extracted with a 10.0 per cent sodium chloride solution in a mechanical shaker. Globulin was precipitated from the extract by the use of ammonium sulfate. The precipitate was washed well and dried in a vacuum desiccator.

Mucoids:[20]

The skin material left after the extraction of globulin was repeatedly washed with dilute sodium chloride solution to remove any remaining globulin. The material was then extracted with half-saturated calcium hydroxide solution in a mechanical shaker. The mucoids were precipitated on acidification of the extract to pH 4.0 with acetic acid. The precipitate was washed well and dried in a vacuum desiccator.

Enzyme Solutions:

The protease was isolated[18] from the fresh latex of madar plants in a crude but highly active form. The solutions of the enzyme in water were freshly prepared for the experiments.

10.0 per cent solutions of diastase (May & Baker Ltd., England) and the

freshly prepared extract[19] of amylase from germinated "ragi" were used for amylolytic studies on mucoids.

As the pH 5.5 was found to be most suitable for unhairing skins and hides by the use of latex of madar plants, the same pH was used for enzymatic studies on the individual skin proteins. Since each of the fibrous proteins prepared viz., collagen, reticulin, elastin, and keratin, and two of the non-fibrous proteins viz., globulin and mucoids, were insoluble in water, enzymatic studies on each of these proteins were carried out as described below. In each case, 1.0 cc. of 10.0 per cent solution of protease from the latex of madar plants was added to 25 cc. of 5.0 per cent protein suspension in water buffered at pH 5.5 by the use of 0.2*M* citrate buffer and the mixture was mechanically shaken for fixed periods in tightly stoppered glass bottles underneath a constant temperature water bath (40°C). Each time a control experiment was carried out under identical conditions except that boiled enzyme solution was used. After the fixed interval, 5 cc of the digestion mixture was taken out, 10 cc. of 20.0 per cent trichloracetic acid was added and filtered. The filtrate was analysed for non-protein nitrogen by micro-kjeldahl method. Although albumin was soluble in water, enzymatic studies on albumin were also carried out in a similar manner. The results are presented in Table I.

TABLE I

Effect of the protease from Madar latex on different skin proteins.

Name of skin Protein	Mgs. of N.P.N. liberated from 1.0 gm. of protein after	
	0.5 hour	4 hours
Collagen	0	0
Reticulin	10	42
Elastin	8	35
Keratin	0	0
Albumin	86	121
Globulin	72	108
Mucoids	51	90

Since amylase also was capable[16, 19] of unhairing skins and hides and since mucoids were found to give a strongly positive Molisch reaction because of the presence of a carbohydrate, the effects of diastase and of the extract of amylase from germinated "ragi" were studied on the mucoids. In each case, the enzyme solution was added to the 5.0 per cent suspension of the mucoids in water buffered at the required pH and the mixture was mechanically shaken underneath a constant temperature water bath (40°C) as before. Each time a control experiment was carried out under identical conditions except that boiled enzyme solution was used. After hydrolysis, the digestion mixture was found to reduce Fehling's solution. A suitable aliquot of the di-

gestion mixture was treated with basic lead acetate solution, made up to 100 c.c., filtered and the filtrate was freed from lead by adding powdered potassium oxalate and filtered. The clear filtrate was quantitatively analysed for total reducing sugars by Lane and Eynon method [25] using methylene blue as an indicator. The results are presented in table II.

TABLE II

Effect of certain amylolytic enzymes on the skin mucoids.

Name of Enzyme used.	pH	Mgs. of total reducing sugars liberated from 1.0 gm. of mucoids after	
		0.5 hour	4 hours
Diastase (M & B)	6.5	60	76
Amylase of "Ragi"	4.5	62	76

Discussion

The results given in Table I show that all the non-fibrous proteins viz., albumins, globulins and mucoids are quite readily hydrolysed by the protease from madar latex whereas, among the fibrous proteins, elastin and reticulin are found to be only slightly hydrolysed and collagen and keratin are found to be affected at all by the enzyme under the experimental conditions. In the practical unhairing experiments also by the use of protease from madar latex, it has been observed that the quality of leather produced is quite good and the hair recovered is quite clean and strong and not damaged. Since collagen is responsible for the formation of leather and since keratin is the chief constituent of the hair, it is obvious that the results obtained in practical experiments with skins and hides as well as in studies with the isolated individual skin proteins are in good agreement. The results also indicate that the process of unhairing skins and hides by the protease of madar latex depends in general on the hydrolysis and removal of the globular proteins.

However, it is not clear whether the enzymic unhairing is caused because of the hydrolysis of only one type of globular proteins viz., albumin or globulin or mucoid or all the three proteins together or any two proteins in combination. On the other hand, amylolytic enzymes [16, 19] also are equally capable of unhairing skins and hides. No proteins are hydrolysed by amylases. No doubt is left with regard to the protein nature of albumins or globulins. The exact nature of skin mucoids, however, has been much debated. Mucoids have been found [24] to contain 12.0 per cent nitrogen and have generally been classed as glycoproteins. On the other hand, they have been found [24] to give a strongly positive Molisch reaction which indicates the presence of a carbohydrate. Considerable confusion exists in the terminology and classification of mucoids exhibiting both protein and carbohydrate function.

Certain experimental evidence indicates that mucoids should be classified as mucopolysaccharides. In mucoids, two components have so far been identified [26], viz., Hyaluronic acid and chondroitin sulfate. Grassman *et al* [27] showed that mucoids contain about 8.0 per cent of glucose and galactose and 1.53 per cent of a hexosamine. Schneider [28] reported that acid hydrolysis of the mucoid liberates equimolecular amounts of glucose and galactose. The mucoids have, therefore, been subjected to the action of certain amylolytic enzymes under properly controlled conditions. The results given in table II show that the mucoids are readily hydrolysed by diastase or amylase of "ragi" with the liberation of appreciable amount of reducing sugars. Such products of hydrolysis have been found to reduce Fehling's solution. The original mucoids however, do not reduce Fehling's solution.

The above results suggest thst the skin mucoids may be considered as some sort of protein-carbohydrate complex the exact nature of which may be described only after more careful and more detailed investigation. Our investigation, however, furnishes strong proof for the supposition that the process of enzymic unhairing by means of proteolytic or amylolytic enzyme depends essentially on the hydrolysis and removal of mucoid material. Mucoids are distributed throughout hides and skins especially at the epidermal-corium junction and around the hair follicles. Naturally, when the mucoids are hydrolysed and removed, the hair-roots are weakened and ultimately the hair becomes loose. Since enzyme bates have been reported [29] to remove mucoids and other globular proteins and since the process of enzymic unhairing also removes such materials, the unhaired pelt by enzymic unhairing may not require any additional bating. This view of the mechanism of enzymic unhairing may also explain to some extent the mechanism of unhairing by the traditional liming process, because lime water is also capable of extracting mucoids from skins and hides. Thus unhairing by the liming process also may in essence be the removal of the mucoid material with a consequent loosening of the hair. The liming process, however, does not remove the mucoids sufficiently as to impart the desired degree of pliability softness to the leather. Limed pelt is, therefore, usually bated to remove the remaining mucoids and other globular proteins.

Summary

(1) With a view to elucidate the mechanism of unhairing skins and hides by the use of proteolytic or amylolytic enzymes, the important skin proteins of both fibrous and non-fibrous type viz., collagen, reticulin, elastin, keratin, albumin, globulin and glycoprotein (mucoids) were individually prepared from skins or hides and the action of protease from madar latex was studied on the individual proteins under properly controlled conditions. The action of diastase or amylase of "ragi" was also studied on the mucoids.

(2) It has been observed that all the non-fibrous proteins viz., albumin, globulin and mucoids are quite readily hydrolysed by the protease whereas some of the fibrous proteins viz., collagen and keratin are not at all digested under the experimental conditions. The other fibrous proteins viz., reticulin and elastin have been found to be only slightly hydrolysed by the enzyme.

(3) It has also been observed that the mucoids are readily hydrolysed by the amylolytic enzymes with the liberation of reducing sugars.

(4) The results indicate that the process of enzymic unhairing by means of proteolytic or amylolytic enzyme depends essentially on the hydrolysis and removal of mucoid material.

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Received Oct. 14, 1954.

Remarks on "An Electrographic Study of Chromium Sulfate Complex Ions"

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In a recent paper by Shuttleworth [1], a number of erroneous statements occur regarding results from ion exchange investigations, including data from one of my papers [2]. He claims that the results of different investigators, who have estimated the charge of the chromium complexes present in solutions of basic chromium sulfates by means of the ion exchange technique are in serious disagreement, which he ascribes to weakness inherent in the method. In particular he states that Adams [3] found that addition of 4 moles per mole Cr_2O_3 of sodium sulfate (about 0.3 moles per liter) had little or no effect on the extent of cationic chromium complexes, while I found [2] that "the addition of one mole per liter of sodium sulfate to a one-third basic chrome liquor caused a drop in cationic complexes from 96 to 55 per cent". Table VIII in Adams' paper [3] shows that the blank solution contains 95 - 96 per cent cationic chromium whereas the solution with 4 moles of Na_2SO_4 per mole Cr_2O_3 showed 85 - 89 per cent cationic chromium complexes. By the same method of operation (H^+ cycle), Grall [4] reports 100 per cent cationic chromium for the blank solution of a salt-free, one-third basic chromium sulfate containing 7.5 g/1 Cr_2O_3. By the addition of 3 moles K_2SO_4 per mole Cr_2O_3, the percentage was lowered to 92 per cent. My own data in the early papers of 1944 [5], and 1946 [6], [7], (Table IV in the last mentioned paper [6]) are: for the blank solution of the 67 per cent acid chromium sulfate ("one-third basic") 96 per cent cationic chromium complexes, and for the solution containing 0.25 mole sodium sulfate per liter (or about 4 moles of Na_2SO_4 per mole Cr_2O_3, which corresponds to Adams' solutions), the cationic chromium was 86 per cent of the total amount of chromium. All the data cited were obtained by the column technique, operated in the hydrogen ion cycle. Finally, by the shaking method, Theis and Thorstensen [8] report for the equilibrated solutions of the one-third basic chromium sulfate, 10 g./1. Cr_2O_3, an amount of 90 per cent cationic chromium for the blank solution and 81 per cent electropositive chromium for the solution to which 4 moles Na_2SO_4 per mole Cr_2O_3 had been added! Hence, the values obtained by four independent investigators for different solutions of basic chromium sulfate of the same type, show surprisingly good agreement, a decrease of the content of cationic chromium complexes by about ten per cent resulting from the addition of 4 moles of neutral sulfate per mole Cr_2O_3. In all instances the addition of sodium sulfate has favored the formation of non-cationic chromium.

By further increase in the concentration of neutral sulfate, the trend of increased formation of non-cationic complexes is accentuated; negatively charged chromium complexes being regular constituents of solutions made one molar in sodium sulfate, although the dominant complexes are *non-ionic*. The figures cited by Shuttleworth from my paper [2], showing a drop of cationic chromium from 96 to 55 per cent, by making the solution of the one-third basic chromium sulfate one-molar in respect to Na_2SO_4 were obtained by the use of the sodium salt of the sulfonic acid cation exchanger, which mode of working eliminates complications due to the action of the H –ions, formed from the neutral sulfate in the H^+ cycle, on the non-cationic chromium complexes. It was particularly stressed in the original paper [2] that high acidity shifts the equilibrium in favor of the cationic complexes, as evident from the data of Table I [2]. By operating the exchange in the hydrogen ion cycle, the corresponding figures were 97 per cent cationic chromium for the blank solution and 66 per cent for the chromium solution of one-molar strength in Na_2SO_4 (Table I [2]). The literature contains only one other investigation of solutions of basic chromium sulfates with such large amounts of sodium sulfate added. In the aforementioned investigation by Theis and Thorstensen [8], 15 moles of Na_2SO_4 were added per mole Cr_2O_3 contained in the one third basic chromium sulfate of 10 g./1. Cr_2O_3 (their Table IV, sample 7), which corresponds to a solution made one-molar in sodium sulfate, the concentration used in the experiment under discussion. Operating the exchange in the H^+ cycle a decrease of cationic complexes from 90 to 58 per cent was found, *i. e.*, an amount of 32 per cent of the total chromium was turned into non-cationic complexes, which compares with a value of 31 per cent (97 – 66) in the corresponding series of my work quoted above. The serious disagreement claimed by Shuttleworth is non-existent. On the contrary, the agreement is excellent between the data of two independent workers. The results are well within the limits of reproducibility claimed for the analysis of chromium sulfates by ion exchange [3], [7].

Further Shuttleworth claims, that "the cationic complexes removed by Adams were found to be about 70 per cent basic as compared with the 40 per cent basicity of the starting liquor, whereas Gustavson's complexes were very little modified in basicity by the exchange resin treatment". This statement is wholly erroneous. Adams' figure on the basicity of the sulfatochromium cations of his neutral sulfate-free solution, or 74 per cent basicity, compares favorably with the values of 72 - 74 per cent (26 - 28 per cent acidity), given in my first paper published on ion exchange of the corresponding basic chromium sulfates [5], [6]. The presence of sulfato chromium cations of the type corresponding to the formula: $(Cr_2(OH)_2SO_4)^{2+}$ in dilute solutions of ordinary chrome sulfate liquors was one of the main findings in the 1944 paper, and therefore it was particularly stressed. In the paper [2] to which reference is given by Shuttleworth, the last heading of Table I [2] reads:

"Per cent acidity of *non-cationic* complexes". Hence, it refers to the *effluent* in which *non-ionic* chromium complexes of the general type $(Cr_2(OH)_2(SO_4)_2)$ were the main constituent. Some minor amounts of anionic complexes, of the type: $(Cr_2(OH)_2(SO_4)_3)^{2-}$ were also present, accounting for the acidity of 69 - 70 per cent found. The non-ionic compound should be 67 per cent acid. Accordingly, Shuttleworth's comparison of the basicity of the *cationic* chromium complexes with that of the *non-cationic* complexes is a serious mistake.

Finally, from the results of his paper-ionophoresis, Shuttleworth draws the following sweeping conclusion: "Although Gustavson has recorded the presence of anionic complexes in the basic chromium sulfates, there was no sign of these on the electrograms. This casts doubt on the use of ion exchange as an accurate tool in chromium complex analysis". It is to be noted that electro-negative chromium complexes (7 to 8 per cent of the total amount of chromium) which I reported, were found only in solutions of basic chromium sulfates made one-molar in sodium sulfate [2]. In the early work [5, 7], the anion exchanger used sorbed small amounts (up to 2 per cent of the total chromium) of non-anionic chromium complexes. However, the figures of 7 to 8 per cent anionic chromium found in solutions of high concentrations of sodium sulfate [2] have been confirmed in subsequent work with the strongly basic quaternary anion exchangers which do not form amine compounds with non-anionic chromium complexes [9]. Also by regular ionophoresis and by paper-ionophoresis, the presence of negatively charged chromium has been demonstrated. The figures for anionic chromium obtained by the method of anion exchange tend to be low compared to the data by ionophoresis. Actually, in solutions of the type given in Table I [2], made one molar in sodium sulfate, boiled and equilibrated, the main part of the chromium does not migrate in the electrical field on short ionophoresis (one hour). Smaller amounts of electro-negative chromium are usually present. The cationic chromium complexes gradually come into the picture on prolonging the time of the ionophoresis, and probably are formed by decomposition of the unstable non-ionic complexes.

Evidently, Shuttleworth has not considered the possibility that his experimental method may be at fault. From considerable experience with ionophoresis of chromium compounds on paper by a method described earlier [10], (an article apparently overlooked by Shuttleworth), the importance of the nature, and particularly the H-ion concentration of the conducting solution must be stressed. It is imperative to keep the pH of the conducting medium as close as possible to the pH value of the solution of the chromium salt under investigation. However, Shuttleworth [1] used 0.05 *M* nitric acid (pH 1.3) as the electrolyte, while a pH of about 3.5 has been found suitable [10], for instance, 0.1 *M* sodium chloride adjusted to pH 3.5. Experience with the cation exchangers in the H^+ and Na^+ cycles already mentioned, shows that the protons liberated in the H^+ cycle convert the non-cationic chromium complexes

into cationic ones to a large extent, even on such short contacts as 10 – 15 minutes. Shuttleworth's failure to find non-cationic chromium was probably caused by the high acidity of his conducting medium, 0.05 *M* nitric acid, which would be expected to convert the non-cationic chromium present in the minute amount of chromium applied in the test into the cationic form. This is surely the case with the non-cationic sulfito-chromium compounds (with a degree of masking > 2 moles SO_3 per mole Cr_2O_3), examined by Shuttleworth and claimed by him to consist entirely of cationic chromium complexes.

The presence of anionic chromium complexes in solutions of ordinary chrome sulfate liquors of high concentration in chrome or neutral sulfate has been proved by numerous workers from the days of Bassett up to the present time. As to literature references and regarding the effect of sodium sulfate on the formation of anionic chromium, the texts of Wilson [11] and Stiasny [12] should be consulted. It is interesting to note that the formation of such complexes is responsible for the non-crystallization of Glauber salt in highly concentrated chrome liquors (about 300 g./1. Cr_2O_3) which may contain amounts of Na_2SO_4 in large excess of its solubility.

Finally, the finding of Plant [13] that concentrated, freshly boiled solutions of chrome alum contain negatively charged chromium complexes entirely, is supported by the X-ray absorption spectrum of chrome alum crystals. The spectrum does not conform to the spectra of the ordinary cationic chromium compounds, for instance the halides. It shows a striking resemblance to the X-ray spectrum of the oxalato-chromiate [14]. Hence, there are indications that the solid chrome alum consists of sulfato-chromiate structures, *i.e.*, a negatively charged chromium complex.

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Received November 1, 1954.

Sole Leather Tanning in a Solvent System

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In a recent review, Whitmore [1] outlined the technical principles on which current sole leather tannage is based; these principles are utilized for the purpose of meeting the merchandising and service requirements of the product to the fullest extent possible. Whitmore [1] properly stressed that the present competitive situation of sole leather producers was at best a difficult struggle, in that their best modern practices were not always sufficient to fully meet the price and serviceability offered by good synthetic soling materials.

At present the sole leather tanner spends approximately 50 per cent of his sales dollar for the purchase of hides. This item is, of course, a major factor in determining a minimum profitable price for the leather. Aside from the exercise of caution and restraint in hide purchasing, there is little that the tanner or the technologist may do to alleviate competitive pressures arising from this factor. However, it should not be overlooked that about 40 per cent of the current sales dollar (approximately equally divided for purposes of discussion) is spent for tanning materials and labor. These are very sizeable items totaling in excess of $8.00 per tanned and finished hide or $8000 daily in a tannery processing 1000 hides per day. It is in this area that the technologist must work to develop possible savings in tanning costs, with concurrent attention devoted to simultaneously achieving improvement in the properties of the product.

If one surveys the situation with a view to determining what information is already available that might be used promptly to attack the foregoing problems, a promising source is the body of information which has been developed during the last 40 years on the principles of tannage in non-aqueous solvents.

O'Flaherty [2] recently reviewed the history and literature of this development; he pointed out that modern chemical engineering could successfully cope with the major problems of safety and economical solvent recovery. He also indicated that an intensive commercial development based on this concept, intended primarily for lighter leathers, was well under way.

The broad general advantages which might accrue from the solvent processing of any type of leather are principally the greater speed and uniformity of tannage and consequent potential savings in labor, inventory charges, etc. The production of sole leather with requisite plumpness, firmness, area yield,

etc. by current methods requires the use of comparatively large quantities of tanning materials and other additives, very long process times (due in large part to penetration problems and economy of tanning materials), and considerable labor and handling in the course of rather prolonged finishing operations.

Therefore, the advantages which are inherent in the solvent processing of leather in general, may apply with singular worthiness to sole leather tannage in a solvent system.

In 1943, Roddy [3] published the results of experimental work which demonstrated that the production of sole leather by solvent processing, using conventional tanning materials, would (in conjunction with usual post-tanning operations) produce sole leather essentially identical to that produced by a conventional rocker yard. The essential features of his procedure are described in the next paragraph.

Raw quebracho extract is the most soluble of the better tannins in suitable solvents. Acetone is a good solvent for the purpose; solutions of approximately 30 percent concentration by weight may be prepared in various ways. When a piece of bated or thoroughly delimed wet hide is placed in such a solution of quebracho in acetone, the tanning material diffuses rapidly and uniformly throughout the hide—this is primarily penetration; fixation to a sufficient degree does not take place in this stage. To obtain acceptable leather it is necessary to take the acetone soaked hide and place it in water for several hours. Fixation of the tannin then occurs, and a very fine and uniformly tanned piece of leather results with a degree of tannage slightly less than 50. Bear in mind that in a conventional rocker yard it is necessary to exceed a degree of tannage of 50 before the hide is completely penetrated and a "slack" tannage is avoided, and this requires from 14-21 days.

The solvent tanned leather is marked by very fine fiber character; it is not cracky, even if lubricants are omitted in later operations, while the original natural grease is either extracted or redistributed (a possible valuable by-product of this process might be the virtual disappearance of the growing incidence of greasy bends).

It is not necessary or desirable to bisulfite the quebracho; furthermore in the acetone tanning system both non-tans and tans penetrate the hide simultaneously so that there is no build up of non-tans in the exterior solutions. The relatively simple procedure proposed by Roddy [3] may be modified to achieve better solvent economy and recovery while eliminating the problems presented by the dilution of the tanning solution caused by contact with the wet hides. If the untanned hide is dried prior to immersion in the acetone tanning solution, this solution will not be altered by the water present in the stock. However, hides in a wet, untanned state cannot be simply dried without severely adverse effects on the character of the hide fiber.

There are several possible ways by which the hides may be adequately dehydrated. One immediately practical method is by sufficient immersion in acetone, followed by evaporation and recovery of residual acetone from the hide, and rectification (in a suitable distilling column) of the acetone water mixture resulting from immersion of the bated stock in the acetone, so that the solvent may be recovered and re-used. Other possible procedures might include freeze drying [4] or the use of possible pre-tannages which would permit simple air drying of the stock without loss of leather making character.

In addition to the advantages which are achieved by avoiding contamination of the tanning solution in the initial dehydration, the time of penetration of the tanning solution through the dehydrated stock is much more rapid than through wet stock. If the dehydrated stock after impregnation by the tanning solution is placed in water, fixation occurs. Here again, recovery of the acetone is complicated by dilution with the water. We have recently observed that at this point the acetone may be evaporated from the hide, condensed and recovered by relatively simple means. The resulting dry impregnated hide is not leather but if it is placed in water, tannin fixation and the conversion to leather occurs in a few hours.

The system thus constituted may require as little as 24 hours total time from beamhouse to first drying. There are thus two immediate advantages—the speed of the process with its consequent economic value, and the ease with which the tanning solution may be re-used indefinitely because of the absence of preferential combination during impregnation and the absence of contamination by water from the raw stock.

However, there are additional potentially important advantages when sole leather is tanned under such conditions. Materials that could not be used because they are insoluble in water, may be utilized in a solvent system, either to improve the properties of the leather or to serve as a replacement for conventional tanning materials.

The amount of tannin which is currently added to the hide to produce sole leather is in considerable excess of the amount required for true tannage or chemical stabilization. A degree of tannage of 20-30 will produce chemical stability, as measured by the shrinkage temperature, equal to the current average figure of 80 if it is properly and uniformly distributed. Much of the excess is presently required to achieve penetration, and some of the tannin contributes to desired bulk and firmness.

Solvent tannage can readily achieve equivalent chemical stability with far less tannin by virtue of the ease of penetration and uniformity of distribution through the cross-section. If other less expensive materials could be utilized to obtain the physical properties and cutting values now supplied by the excess tannin, substantial dollar savings are quite possible.

In line with this concept, we have experimented with various low-cost resinous materials which are available in large quantities. These materials are insoluble in water, but soluble in acetone and other organic solvents. These resins may be dissolved in acetone together with quebracho and they will penetrate the hide simultaneously with the quebracho to ultimately produce leathers which are very similar in appearance and character to conventional sole leather.

The properties of this leather may be varied by changes in the relative proportions of quebracho and resin; it appears quite likely that considerably less finishing materials and labor will be required for such a leather. All the physical tests and very limited wear tests that we have conducted to date indicate that this type of leather is at least equal in performance to conventional sole leather. Only larger scale production and testing can reliably settle this point.

Leather produced in this manner has a content of combined material equal to a degree of tannage of 40-45, with practically no freely water soluble material. Ordinarily 100 lbs. of pure dry hide substance will make from 275 to 300 lbs. of sole leather. In the new procedure suggested here, 100 lbs. of such hide substance will yield only 140-150 lbs. of leather. As a consequence, the specific gravity is less than 0.7, compared to more than 1.0 for usual sole leather. A lighter weight sole may be a very valuable merchandising asset.

Obviously this leather cannot be sold on a weight basis, but must be offered on an area basis, within any given thickness classification. If it is sold on such a basis, which is essentially true cutting value, the less mass we add to the hide substance the less the cost of tanning will be. When less material is used, and a substantial portion of that would cost only a fraction as much as conventional tanning materials, consistently large savings may be a real possibility. This can be verified by anyone who wants to take the trouble to compare the costs of materials in sole leather with a typical present day chemical analysis against a projected new leather having a composition equivalent to 40 lbs. of material on 100 lbs. of hide substance with a substantial fraction of that 40 lbs. costing as little as $0.05 per lb.

Substantial savings are absolutely necessary to justify the considerable expenditure that would be required for engineering development, and eventual new process equipment, including safety features, recovery still, etc. These savings must be sufficient to promise reasonably prompt amortization of a substantial capital investment, and to compensate for reasonable, but inevitable solvent losses; in addition it must be a process which is producing leather with relatively undiminished cutting value in spite of its light weight. Technically the outlook for good solvent recovery is excellent, and this also appears to be true of the prospects for maintaining cutting values from a given hide, although at least small scale production experience is required before adequate assurance on this vital matter can be obtained.

There are other potential savings which in the aggregate would be substantial in terms of daily dollar savings:

a. elimination of rocker yard and layaway facilities, with resulting reduction of inventory and labor in tanning.
b. the possible reduction of finishing time and labor.
c. simple process control, relatively small batch size (or possibly a continuous process) which would permit prompt awareness of any trouble developing, trouble which would be confined to a limited number of hides.
d. reduction of that part of the sewage disposal problem caused by tanning operations.
e. possible merchandising benefits resulting from the increased versatility of the procedure and its ability to meet changing market requirements promptly.
f. future research to permit incorporation into the tanning mixture of relatively small amounts of added materials designed to increase wear, water resistance, and possibly to upgrade less profitable areas of the hide.

There are numerous engineering and subsidiary problems and details to be worked out, but there do not appear to be any fundamental difficulties which would block the ultimate success of such a drastic change in processing. As examples of the problems involved, a major consideration is safety, both for personnel, and for the satisfaction of the requirements of underwriters and applicable laws and ordinances. It may be necessary and desirable to blanket all operations with an inert gas, which fortunately is not too costly a proposition, as producer gas units are available whose chief product is nitrogen supplied free from the air used for the combustion of a cheap fuel under controlled conditions.

Other problems include development of suitable means for dissolving the tanning materials in the solvent on a large scale, the preservation of cutting values, the means of assuring uniform and reproducible dehydration which is indispensable to the final desired properties of the leather, the carrying out of all operations involving solvents at the greatest possible speed, so that the effective daily capacity of any unit is thereby increased with smaller unit investment required.

The above considerations certainly seem to warrant further development work, as such a process offers a basis for a promising attempt to materially reduce processing costs while being able to widen the range of products to be produced. Such an effort would permit the tanner to improve his position in the principal cost brackets which are under his direct control, and which are costly enough to allow worthwhile savings.

Acknowledgment

The technical assistance of Mr. R. Lee Southwood has contributed materially to the information outlined here. The interest and counsel of the Director and staff of the Tanners' Council Laboratory and the financial support of the Sole Leather Group of the Tanners' Council is acknowledged with sincere appreciation.

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Received October 1, 1954.

BOOK NOTICE

An Introduction to Industrial Mycology. Fourth Edition. By George Smith. Edward Arnold (Publishers) Ltd., London. Submitted by St. Martin's Press, Incorporated, New York. 378 pages, cloth $6.00.

This book, in its fourth edition, offers a relatively clear and precise indoctrination to the field of industrial mycology. The tannery chemist and those in the tanning industry not specially trained in mycology will find the book a good starting point in becoming familiar with the names and general identification of some of the molds and yeasts found in the tannery. Over 160 illustrations are given to familiarize the reader with characteristics involved so as to aid in identification. The chapter on the control of mold growth shows the need of control and discusses some antiseptics which have been found useful. The use of paranitrophenol for leather and its effectivity is covered. W.T.R.

ABSTRACTS

The Chromatographic Separation of the Diastereoisomerides of Lanthionine. By S. Blackburn and G. R. Lee. *Chem. and Industry*, **No. 41**, 1252 (1954.) The principal product formed from the cystine residues of keratins or other cystine-containing proteins when they are treated with alkaline solutions is lanthionine; the possibility of the occurrence of other types of reaction, however, has been suggested. The authors found need for a direct method for the determination of lanthionine since no reliable method has previously been reported. The present method is based on the chromatographic separation and subsequent colorimetric determination of the lanthionine. The mixture of amino-acids, or the protein hydrolysate, containing lanthionine to be analyzed is applied to a 100 x 0.9 cm. column of the ion-exchange resin Dowex 50 according to the procedure of Moore and Stein. The

column is developed with the pH 3.42 buffer only and the eluate collected in 1-ml. fractions. Lanthionine emerges from the column in the region between serine and glutamic acid. The amount of lanthionine in the fractions is estimated by reaction with ninhydrin at pH about 1, rather than by using the Moore and Stein reagent. This modification renders the reaction more specific for lanthionine. To each 1 ml. fraction in the test tube is added 1 ml. of glacial acetic acid and 1 ml. of ninhydrin reagent, prepared by dissolving 2.5 g. of ninhydrin in a mixture of 40 ml. of 6M- phosphoric acid and 60 ml. of glacial acetic acid. The stoppered test tube is then heated for 10 min. in a vigorously boiling water bath. The reaction mixture is diluted with 2 ml. of glacial acetic acid and the optical density of the solution measured at 455 mμ against a blank consisting of 1 ml. of buffer solution treated in a similar way. The amount of lanthionine present in the fraction is then read directly from a standard curve. The relationship between optical density and concentration is essentially linear for amounts of lanthionine up to 45 mg. per ml. Proline and lysine both give colored solutions when treated with ninhydrin in this way, but emerge from the column later than lanthionine and cause no interference. When a mixture of L- and meso-lanthionine is applied to the column, two incompletely separated peaks corresponding to the two isomerides, are observed. Complete separation of the peaks is obtained using a column of dimensions 300 x 1 cm. operated at room temperature. A separation of L- from D-lanthionine on these columns is hardly to be expected. Among similar separations of diastereoisomerides which have recently been reported are those of the diastereoisomerides of hydroxylysine, isoleucine. hydroxyproline, and threonine.

Chromium in Liquors and Leather. By P. S. Venkatachalam. *Bull. Central Leather Research, Madras.* Through *Lea. Trades Rev.*, **115,** 133 (1955). After a review of the several methods for the determination of chromium in leather and tan liquors, the author settled on the lead peroxide method. Details of the method follow. (a) Liquors. 50 ml. of liquor of concentration 0.10 per cent chromium, are taken in a 250 ml. Erlenmeyer flask to which 1.0 ml. of 36 *N* H_2SO_4, followed by 1.0 gm, lead dioxide, are added and boiled vigorously for not less than 15 minutes. A funnel with bent stem is kept over the mouth of the flask to prevent loss by spurting. The flask is removed and contents are cooled and made to 200 ml. in a standard flask. The liquor is filtered through a Whatman No. 4 filter paper and 100 ml. of the filtrate are titrated iodimetrically or against ferrous ammonium sulfate, using a Serfass titrimeter. (b) Estimation of chromium in leather. One gm. of leather is taken in a Erlenmeyer flask and 5.0 ml. 36 *N* sulfuric acid are added and the whole is heated gently until the contents are completely charred. After cooling, 15 ml. of 16 *N* nitric acid are added and the flask gently warmed until the carbon is oxidized and the solution assumes a greenish blue color. Heating is continued until all the nitrous fumes are expelled and the sulfuric acid fumes copiously. The solution is cooled, diluted to about 50 ml. with water and boiled vigorously with 2.0 gms. of lead dioxide. The rest of the procedure is as under (a).

In all, about 15 ml. of nitric acid are required for the oxidation of the carbon. Semi-chrome and chrome retanned leathers require a few more ml. of nitric acid for complete oxidation. Wherever possible, boiling with lead dioxide might advantageously be extended to 20 minutes. The critical conditions that have to be observed are (1) time of heating after oxidation sets in, as judged by sudden change in color of contents to orange, should not exceed two minutes for liquor and three minutes for leather. (2) loss of chromium as volatile chromyl chloride is checked by using a funnel to cover the mouth of the flask. (3) formation of peroxide is avoided by sudden chilling of contents under a tap, and (4) removal of chlorine by boiling off at least ten minutes. Conditions (3) and (4) are easily observed and errors creep in generally if (1) and (2) are not obeyed. Excepting (1) all other conditions are easily followed and any error due to them is avoided.

Utilization of Sulfite Cellulose Waste Liquor as Tanning Material. I. Chemical Composition and Its Purification. By Y. Sakimoto. *Jap. J. Zootech. Sci.*, **22,** 73 (1952). The waste liquor produced by the calcium bisulfite digestion method was sampled from the digestor and analyzed. Its analysis in per cent was as follows: tannin 5, total solids 12, total ash 1.2, free SO_2 1.2, CaO 0.67, Fe_2O_3 0.01 - 0.1. After passing through a tower for the removal of free SO_2 the original sulfur dioxide content of the waste liquor was reduced to 0.3 per cent and by open evaporation it was reduced to 0.1 per cent. Solids were increased by the open evaporation to 55.3 per cent. By adding sulfuric acid equivalent to the lime content of the waste liquor the lime and total ash content decreased by 58 and 33 per cent respectively and tannin increased by 56 per cent. The removal of iron with sodium carbonate was greatest at pH 9, but even here only one-half of the iron was removed. For complete removal of the iron, twice as much sodium carbonate was required and the pH consequently rose to 11. In tanning chromed hide powder with the foregoing purified liquor, it was found that calcium magnesium and iron oxides, free SO_2 and sulfonic SO_2 were all adsorbed by the hide powder, but the adsorption of lime was less in comparison with the iron.

Utilization of Sulfite Cellulose Waste Liquor as Tanning Material. II. On the Preferential Tannin Absorption by Hide Powder From Blended Tan Liquor. By Y. Sakimoto and K. Katayama. *Jap. J. Zootech. Sci.*, **23,** 174 (1953). Different tanning materials when used separately are absorbed by hide protein at different speeds. The question arose as to whether they are also taken up at different speeds from mixtures. The authors applied their bichromate oxidation method of tannin estimation to this problem. The blends used were (1) chestnut and wattle, (2) chestnut and mangrove, (3) chestnut and sulfite cellulose and (4) sulfite cellulose and Mertanol 7AN. In the first case there was no preferential absorption at pH 3.95 and 3.00. In the second case, chestnut was preferentially absorbed at pH 4 and 4.9. In the third case, vigorous preferential absorption of tannin was noted at pH 5.2 and 3.43. In the fourth blend, the sulfite cellulose was preferentially absorbed at pH 2.2, but proportionally absorbed at pH 3.5. The authors conclude that the preferential adsorption of tannin by hide protein is mainly concerned in the properties of the materials blended and that preferential absorption can be repressed or facilitated by the adjustment of the pH of the tan liquor.

Utilization of Sulfite Cellulose Waste Liquor as Tanning Material. III. On the Salting Out of Blended Tan Liquor. By Y. Sakimoto and K. Katayama. *Jap. J. Zootech. Sci.*, **25,** 45 (1954). The influence of blending on two different kinds of tanning extracts on the dispersion of tannin particles in the blended liquor was studied by means of the fractional salting out method. The authors also examined the fractional salting out of individual tan materials and observed the changes of ratio of both components of the precipitated fraction by means of their dichromate oxidation method for tannin estimation. The results are summarized as follows: (1) In the case of single tan liquor the amount of tan which was precipitated by fractional salting out increased with decreasing pH value. (2) The chestnut and sulfite cellulose blend, adjusted to pH 4.6, and sulfite cellulose and mangrove blend, adjusted to pH 4.1, showed remarkable increase of the lyophobic fraction. The lowering of the degree of dispersion of chestnut and mangrove blend adjusted to pH 4.4 did not show the same increase, but in this case the pH was higher than the original 3.5. In general, lyophobic fractions were increased by blending, especially when sulphite cellulose formed one of the constituents. (3) The amount of tannin salted out from the two constituents of a blend was found to bear no relationship to the tannin content of the original material.

On the Bichromate Oxidation Method for Tannin Estimation. By Y. Sakimoto and K. Katayama. *Jap. J. Zootech. Sci.*, **22,** 95 (1952). The permanganate titration method of tannin estimation with indigo carmine as indicator is not too accurate because of the difficulty in securing a sharp end point. In order to obtain a more accurate volumetric method the authors devised the bichromate method, using gallic acid as the standard. Other tanning materials are evaluated with respect to the gallic acid factor. The authors found that the amount of bichromate reduced by the tannin quite accurately corresponded to the tannin estimation by the official hide powder method.

On the Phosphorous Pentoxide Fixation by Gelatine and Metaphosphate Pretanning of Vegetable-Metaphosphate Combination Tannage. By Y. Sakimoto. *Jap. J. Zootech. Sci.*, **24,** 180 (1954). At pH 2.3 - 3.6 the fixation of P_2O_5 was the greatest. The metaphosphate concentration effect on P_2O_5 fixation by gelatine was highest and nearly constant at a concentration of 0.01 - 0.1 mol P_2O_5. The P_2O_5 fixation increased with gelatine concentration. The higher the reaction temperature rose, the lower was the P_2O_5 fixation. Hide powder previously tanned with vegetable tannins was able to fix less P_2O_5. Hide powder previously tanned with metaphosphate was able to fix less vegetable tannin.

Observations on the Collagen System. Sixth Proctor Memorial Lecture. J. T. Randall. *J. Soc. Leather Trades' Chemists*, **38,** 362 (1954). Randall's review stresses biological and biochemical studies of collagen fibrogenesis, x-ray diffraction and electron microscopic studies of collagen structure and some problems of the solution and precipitation of collagen in vitro, with particular emphasis on an integrated outlook. Recent research within his own research group is also reported. Collagen fibrogenesis studies concerned with cellular filaments and granules are described. Tissue culture studies of collagen forming fibroblasts as well as osteoblasts indicate that a polysaccharide rich, protein containing component is found in the granules. Though electron microscopic examination did not detect typical collagen fibrils, the amino acid composition of the protein was rich in proline, hydroxy proline and glycine. Regardless of the conclusions about the origins of the observed connective fibers, it is observed that they continue to develop outside of the cell. The development of collagen is a gradual process. Full 640 Angstrom periodicity is not observed in rat tail tendon collagen until the rat is three weeks old. In the earliest, or embryonic, stages, globular forms are noted, followed by a 210 Å. fibrillar form which precedes the conventional fibrillar form. High and low angle diffraction studies of collagen are included. Fiber extensions up to 10 per cent have a more marked effect on the low angle diffraction pattern than on the high angle pattern. It is concluded that the high angle spacing is linked to the elastic component of fiber extension. Detailed examination of over 100 molecular models has been made in attempting to find a model which satisfies all available data. A note added in proof describes a two strand helix, each having a lead of 8.7 Å., with the pitch of the helix being 4.35 Å. The structural repeating unit contains four residues with a total projected fiber axial length of 6 Å., the two strands being related by a screw axis such that the repeat is 3 Å. Further work is in progress, but the model conforms reasonably well to the several criteria for collagen structure. Precipation studies on collagen gels have shown four gel types:

(a) - Gels, showing no ordered structure.

(b) - Fibrous precipitates of collagen induced by simple salts and/or pH changes.

(c) - Fibrous precipitates induced by complex polyelectrolytes such as acid glycoproteins, the precipitates showing characteristic long periods in electron microscopic examination, which precipitates have been called "fibrous long spacings."

(d) - Precipitates induced in vitro by adenosine triphosphoric acid, yielding short fibrillar lengths, called "segmented long spacings."

The role of van der Waals and electrostatic forces in the mechanism of fibril formation is considered. It is suggested that the latter two precipitate forms should not be spoken of simply as collagen when it is shown that the precipitate formed also includes the precipitate inducing agent. Further, the coincidence of the stereochemistry of collagen and of the precipitating molecule seems important. Ultimately, it is hoped that a knowledge of the mechanism of collagen precipitation may suggest mechanisms for collagen fibrinogenesis in vivo. R.M.L.

The Preparation of Hide Powder. By A. Küntzel and H. J. Kurth. *Das Leder*, **5**, 237 (1954). The filter method of tannin analysis depends on hide powder of uniform properties such as uniform absorption of tannin, swelling, and release of soluble protein or mineral matter. Specifications for hide powder usually list chemical behavior, soluble matter, pH, ash, and chrome content but not state of division. The last, however, is difficult or impossible to define. After World War I, when Freiberg hide powder could not be obtained, each country made their own powder and very different products appeared. For example, a coarse powder contained horny granules that could only be held in the filter bell with cotton, and 7 grams, when packed tight enough to give the proper flow of tannin solution, filled only half of the filter bell. Structural differences in the powder influence the tannin results less for natural tannins than for tannins of low astringency such as lignin sulfo acids or syntans. Manufacture of hide powder was formerly a secret process but now anyone with some effort can make it, although little can be found in the literature regarding the methods. Chambard (*Rev. Tech. Ind. Cuir*, **37**, 1945) reported a complete method for making chromed hide powder. An increase in precision of the hide powder method is not possible until either a single source of hide powder is established or the various types of powder can be made uniform. The latter will necessitate discussions and exchanges of ideas. The Darmstadt Institut fur Gerberei-Chemie has been charged by the West German leather industry with preparation of hide powder. Work has been done on grinding as well as on chemical preparation of the hide. The principal difficulties in chemical treatment of hide are found in making prechromed hide powder, therefore the manufacture of only this type is described below. Preparation of unchromed powder then presents no additional problems. *Grinding.* The sample must not be heated too much during grinding. Three types of mills are illustrated. The Brabender mill is essentially the same as the American Wiley mill. It should be used with a 0.5-0.6 millimeter screen. It operates well only when suction (vacuum cleaner may be used) is applied below the screen; this influences fineness and the time the hide material is in the mill. The material fed to the mill must not be more than 2 millimeters thick and only a few square centimeters in area. To precut the sheets of split hide, a machine was devised which consists of a series of circular knives separted by notched feed rollers. It rapidly cuts the hide splits into narrow strips. The capacity of the Wiley mill is only 1 kilogram in 3 or 4 hours. With a coarse screen it may be used to precut the hide material for grinding in other mills. The Grumbach mill (which has a hinged door and general design similar to the Wiley mill) has a water cooled housing and door. Four rotating knives operate against the stationary, rasp-like upper half of the housing. The lower part of the housing has a 0.5-0.6 millimeter screen. The material fed to the mill must be precut to pieces not more than 0.5 sq. cm. in area, otherwise it will remain in the mill too long, lose its fibrous character, and become grainy or gritty. This mill must also have suction under the screen and the ground material should be collected in a cyclone separator. The fresh air sucked through the mill gives additional cooling so that the mill does not heat on long grinding. At 700 r. p. m. the mill will grind 1.5-2 kilograms of hide powder per hour. Recently the firm, Alpine A. G. Maschinenfabrik, Augsburg, has put on the market a hammer mill based on the latest techniques. This Superplex-Kühlstrommühle is especially suitable for hide powder. Other mills cut or rasp the hide and so produce short fibers, whereas this mill

subdivides the material by beating it in air with rapidly rotating hammers. The hide powder so produced is long-fibered, uniform, and cottony. The screen forms the grinding chamber outer wall. Using a screen with holes 0.5 millimeters in diameter results in hide powder of which 5.5-6 grams will entirely fill the filter bell. The bell thus filled has the same absorption as when filled with 7 grams of Freiberger or Darmstadt powder. The mill is made in two sizes; the smaller mill will grind 25 kilograms of hide powder per hour. The yield is best when the machine is fed material precut to 3-5 milimeters. This company makes a "Rotoplex" cutting mill suitable for precutting hide for feeding to the hammermill. In conclusion it may be stated that there are mills on the market by means of which hide powder of any desired finess can be made. Structural differences in various commercial hide powders can therefore be avoided. *Chemical pretreatment of the hide material.* Two methods for preparing the hide material are given, one using limed and the other unlimed hide. The best raw material from the standpoint of availability and cost is heavy bull hides or bull necks. The hide may be either fresh or salted, but must be thoroughly soaked and well fleshed. The hide should then be split to remove completely the papillary and flesh layers. The flesh split must be thick enough to remove all material high in fat, otherwise the powder may be difficult or impossible to wet. It is not advisable to use splits from a tannery, as these may not have been suitably handled to remove fat. The middle layer should be split into layers about 2 millimeters thick. Splitting before liming results in rapid, uniform liming. Experience has shown that liming for 2 days in a white lime is sufficient. Liming for too long a time makes it difficult to secure a uniform chrome tannage. After liming the hide must be thoroughly rinsed, carefully delimed (for example with Cavit) and again rinsed. In the chrome tannage it is important that the inner layers be tanned. If only the surface of the split is tanned, then after grinding, a mixture of chromed and unchromed powder will be obtained. Because of liming the unchromed material will give up soluble protein and lead to high nontannin values. Chambard, in order to get uniform chroming, dehydrated the delimed hide with acetone, ground it in a mill, rewet it to chrome it, then again dehydated the hide material with acetone, dried it in the air and finally ground it to finished hide powder. His process is too troublesome and costly for large scale production. A uniform thorough tannage has been obtained by (a) splitting the raw hide very thin, (b) pickling with 2 percent hydrochloric acid before tanning, and (c) by adding the chrome solution slowly in 3 portions. The chrome tanning agent was 0 percent basic chromic chloride, using 0.8 percent, on white hide weight, of the hexahydrate, $[CrCl_3 \cdot 6H_2O]$. After tanning and neutralization to pH 6, the finished hide powder will contain 0.6-0.7 percent of Cr_2O_3. Neutralization to this high pH value is necessary in order to prevent swelling during rinsing, otherwise complete removal of soluble matter would be prevented. Rinsing is complete when practically no chloride ion can be detected in the rinse water with silver nitrate. The chrome content can vary within certain limits. Proposals for the analytical control of hide powder stress chrome content, but the latter does not have the influence on quality ascribed to it. Variation in chrome content influences only the swelling properties of the powder and has no influence on tannin absorption. Increasing chrome content results in decreased swelling so that the tannin solution passes through the hide powder column more rapidly during the analysis. The purpose of chroming is to decrease the soluble protein fraction, and sufficient insolubility is obtained with 0.3-0.4 percent Cr_2O_3, based on the weight of dry hide powder. The chromed, thoroughly rinsed splits should be acidified with formic acid. This step is necessary in order to get optimum tannin values with syntans, as these are difficult to detan. Pure natural tannins, on the other hand, give the same nontannin values regardless of the pH value of the hide powder. The dilute acid should be added in portions in a float of 200 percent. Acidification is complete when the pH value of the float is 4.8 two hours after the last addition of acid. Acidification must not be carried too far otherwise the powder will swell and so hinder or prevent the flow of tannin solution through it during the detanning operation in the filter bell. The acidified hide splits should

then be pressed or centrifuged, tacked out and dried. The preparation of hide powder from unlimed hide is much simpler than from limed hide, because the former can be chromed at once after splitting and without pickling. Unlimed hide takes up the chrome solution more slowly than limed hide, so that uniform penetration is more easily obtained. Neither pickling nor neutralization with bicarbonate is needed. The chromed pieces, however, should be left on a horse for two days before rinsing. They should be acidified in the same way as for limed pieces; the end pH value of the float should be 4.8. The two hide powders, prepared as described above, are entirely equal in their behavior in detanning solutions of vegetable and synthetic tannins. A difference in behavior was found only during grinding. Hide powder from unlimed hide was not as voluminous as that made from limed hide. However the process with unlimed hide is preferable because it is a simpler process and also has the advantage that no variation in hide powder quality will be introduced by variations in the liming procedure. If the Augstburger Kühlstrommühle is used both types of hide material will give the same type of hide powder, because of the great fiber splitting action of this mill. It is hoped this publication will initate an exchange of experiences, that will result in a uniform method for making chromed hide powder. I.D.C.

A Simple Rapid Method for Determining the Dyeing Behavior of Anionic Dyestuffs. By G. Otto. *Das Leder*, **5**, 244 (1954). The following rapid method for evaluating anionic dyes makes use of the standardized, weakly chromed hide powder which is available in every tannery laboratory. Measure by eye 1 cc. of the hide powder (loosened by shaking) into a test tube. With practice it is soon possible to measure out uniform amounts of about 0.065 grams within 10 percent. Pipette onto the hide powder 10 cc. of water, acidified with sulfuric acid to pH 3.7, shake, then add 6 drops (approximately 0.25 cc.) of a solution containing 5 grams per liter of the dyestuff to be tested. Shake the tube a half minute. To a funnel 5 cm. in diameter, add a small amount of glass wool to cover the exit and pour the suspension of hide powder slowly through the funnel, collecting the filtrate in a second tube. Repour the filtrate through the funnel until it is optically clear, — this may require 12 to 20 returns of the filtrate. The tube with clear filtrate (Tube I) is then set aside. The dyed hide powder is washed on the funnel with dilute alkali, pH 8.3, prepared by adding 1 cc. of 1 percent ammonia solution per liter of water. Add this solution slowly from a pipette, collecting the wash solution in a third tube; repour twice, then collect in a fourth tube, (Tube II). Compare the color of Tube I with a tube containing 10 cc. of the acidified water (pH 3.7) to which one drop of the dye solution (5 grams per liter) has been added. Compare Tube II with a tube containing 10 cc. of the ammoniacal solution (pH 8.3) to which a drop of dye solution has been added. The following table lists 8 groups of dyes based on their behavior in the test:

Group	Color (as compered with control)		Dyeing action on fresh chrome leather
	Tube I	Tube II	
1	none	none	surface only
2	none	weak, to 30% of control	uniformly colored
3	distinct, to 50%	very weak, to 10%	as in 1 but with small proportion of penetrating dye
4	weak, to 30%	weak, to 30%	slightly stronger than 2
5	weak, to 30%	moderate, to 50%	uniformly through grain
6	moderate, to 50%	strong, 100%	almost through
7	strong, 50-100%	very strong, over 100%	through
8	very strong, over 100%9	very strong, over 100%	through, bleeds readily

The above grouping does not apply for anionic dyes on vegetable tanned leather. With vegetable leather there is little difference between group 2 and group 6. Brush dyes of

group 2 penetrate through vegetable leather, whereas group 6 dyes do not. Results with freshly chromed hide powder were not as satisfactory as those with the prechromed powder. I.D.C.

Salt Stains-Bacterial Stains. (A Discussion of the Cause of Stain Formation). By W. Hausam. *Das Leder* **5,** 247 (1954). Salt stains are formed according to Küntzel and Stirtz (*this Jour.* **49,** 694) by the reaction of alkaline earth compounds from the curing salt with autolytic decomposition products of the blood. Many factors, however, indicate bacterial action is a factor. The salt used on a heavy hide contains a much greater amount of alkaline earth compounds than the salt on a calfskin, yet calfskins are stained more than heavy hides. Alkaline earth salts favor bacterial growth. True disinfectants, such as cresol, phenol or zinc oxide, reduce staining. Stains are found almost exclusively under poor salting and storage conditions and can be prevented by careful salting, storage and handling. I.D.C.

Reply to the Preceding Statement by W. Hausam "Salt Stains-Bacterial Stains". By A. Küntzel and T. Stirtz. *Das Leder,* **5,** 251 (1954). Middle layer stains are free from bacteria; autolysis was therefore suggested as the cause of blood decomposition. Flesh and grain stains are identical with middle layer stains, therefore the same cause was assumed for each. The suggested mode of formation was given as a working hypothesis and not as a proven theory. Disinfectants may prevent stains but, on the other hand, without disinfectants, staining may not occur. Stains are very difficult to produce in the laboratory. Chambard (Festnummer Österr. Lederzeitung 1954) for example was unable, in the laboratory, to produce stains on a sound hide. I.D.C.

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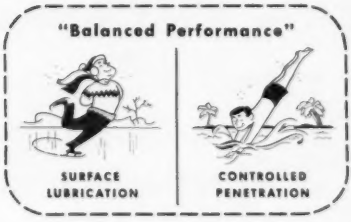

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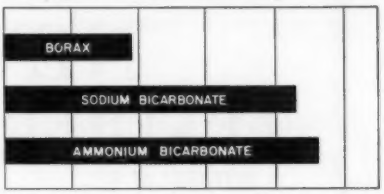

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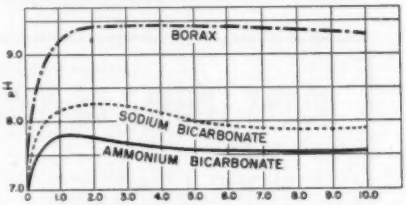

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ITALIAN

CHESTNUT EXTRACT

Solid — Powder — Spray Dried

also

MELLOWED CHESTNUT

Highly Soluble — Weight Giving — Good Color

MADE FROM LIVE WOOD

TYPICAL A.L.C.A. ANALYSIS

	Solid	Mellowed Powder	Spray Dried
TANNIN	61.72	65.95	73.5
NON-TANNIN	21.65	26.67	19.1
INSOLUBLES	.65	.67	.7
WATER	15.98	6.71	6.7

STAINLESS SUMAC CRYSTALS

CIPEC

HIGHEST QUALITY—MADE UNDER THE SUPERVISION OF THE WORLD'S LEADING EXTRACT CHEMISTS

SOLE AGENTS

TANEXCO, INC.

549 W. Washington Blvd. Chicago, Illinois

MYRTAN

A TANNING EXTRACT

made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

TYPICAL A.L.C.A. ANALYSIS

	Ordinary	Clarified
TANNIN	61.55	64.34
NON-TANNIN	16.03	17.14
INSOLUBLES	1.70	0.72
WATER	20.72	17.80

Also Available as Liquid with 30% Tannin

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

Blended into sole leather tannages, it has given better yields and improved color.

For further information address:

TANEXCO, INC.

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SPECIAL DIPPING EXTRACTS
RAPID TAN "G"

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AMERICAN EXTRACT CO.

Manufacturers of the Largest
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Established 1887
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